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MOLECULAR VOLUMES AND EXPANSIVITIES OF LIQUID NORMAL HYDROGEN AND PARAHYDROGEN

By Russell B. Scott and Ferdinand G. Brickwedde

ABSTRACT

The molecular volumes at saturation of liquid normal hydrogen and parahydrogen between 14° and 20.4°K were measured with a fused-quartz dilatometer, the amount of hydrogen being determined from the pressure of the gas in a calibrated flask at a measured temperature. The results are represented by the equations:

$$V(n\text{-}H_2)\ \text{cm}^3\ \text{mole}^{-1} = 24.747 - 0.08005T + 0.012716T^2$$
$$V(p\text{-}H_2)\ \text{cm}^3\ \text{mole}^{-1} = 24.902 - 0.0888T + 0.013104T^2$$

At the normal boiling point of n-H_2 (20.38°K), $V(n\text{-}H_2) = 28.397 \pm 0.010$ and $\Delta V(p\text{-}n) = 0.138 \pm 0.010$. The expansivity of p-H_2 is only slightly greater than that of n-H_2.

The change observed in the molecular volumes of H_2 in passing from the state in which the molecules rotate (o-H_2) to the state in which they do not rotate (p-H_2) is opposite in direction to the change observed in other substances when passing between these two states of molecular rotation and nonrotation. The changes in "lattice" energies are also of opposite sign. It is shown that the random state of orientation of the axes of p-H_2 molecules makes the state of nonrotating p-H_2 fundamentally like that of rotation in other substances at high temperatures.

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I. INTRODUCTION

Some recent investigations of X-ray diffraction, dielectric constants, and specific heats show that the molecules of a number of substances in a condensed phase are oriented. These experiments have shown also that at a certain temperature, characteristic of the material, the oscillatory motion of the molecules about the direction of orientation changes to molecular rotation. This change is accompanied by an increase in molecular volume and in the energy of the condensed phase (hump on the specific-heat curve), the state of molecular rotation having the larger volume and larger energy.

In liquid parahydrogen, p-H_2, below 20°K, there is no molecular rotation since practically all the molecules are in the state whose rotational quantum number, j, is 0, whereas in liquid orthohydrogen, o-H_2, ($j=1$) there is "free" molecular rotation, which is demonstrated by the fact that the difference in energies of the rotational levels is the same in the liquid and gaseous phases.[1] The variation with

[1] J. C. McLennan and J. H. McLeod, Roy. Soc. Canada, Trans. 23, section 3, 19-20 (1929).

temperature of the difference in vapor pressure of these two forms of hydrogen reveals a difference in the "lattice" energies of the condensed state, and one is led to expect a difference in molecular volumes also. The condensed state of *o*-H has the lower "lattice" energy although it has the greater total energy, and it has now been found that it has also the smaller molecular volume. Thus it is seen that in the case of liquid hydrogen, the change from the state in which the molecules do not rotate (p-H_2) to the state in which they do rotate (o-H_2) is accompanied by a decrease in the molecular volume and "lattice" energy of the condensed state. *This is opposite to the direction of the change in the other substances that have been investigated.*

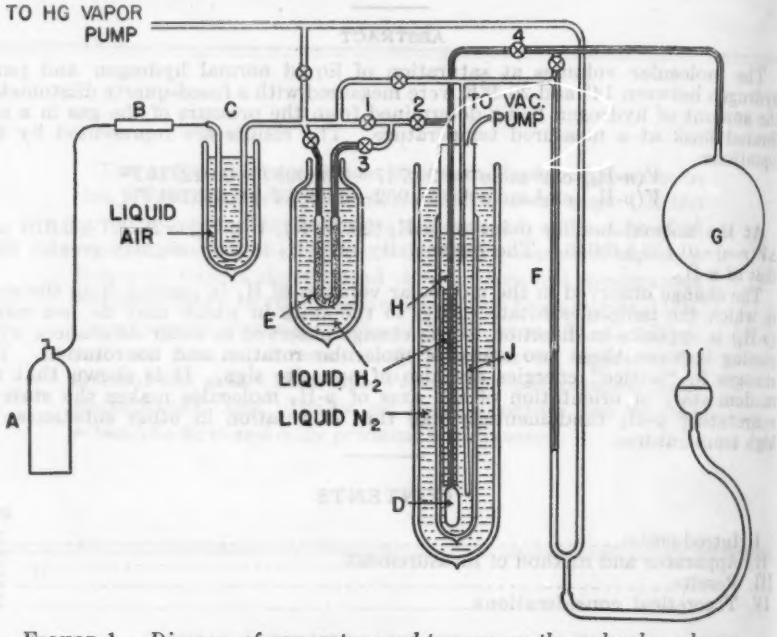

FIGURE 1.—*Diagram of apparatus used to measure the molecular volumes.*

A, cylinder of hydrogen; *B*, tube containing copper gauze; *C*, U-tube containing cotton; *D*, dilatometer; *E*, catalyst; *F*, Hg manometer; *G*, 3-liter calibrated flask; *H*, fused-quartz capillary; *J*, vapor-pressure tube.

It will be brought out in the discussion that the condensed state of nonrotating p-H_2 is fundamentally like that of molecular rotation in the other substances investigated, the state of rotating o-H_2 corresponding to the state of molecular orientation in other substances.

The measurements were made on normal hydrogen (75 percent o-H_2), and 20.4°K temperature equilibrium hydrogen (99.8 percent p-H_2).[2] Careful measurements of the density and expansivity of liquid hydrogen had previously been made by Onnes and Crommelin,[3] but these measurements were made before the ortho and para forms of H_2 had been discovered, whereas it is now known that liquid normal H_2 changes at an appreciable rate by conversion of the ortho constituent into p-H_2. The molecular volume and expansivity of liquid normal H_2 were, therefore, carefully redetermined. The molecular volume and expansivity of liquid p-H_2 were measured in the same apparatus.

[2] Harkness and Deming, J. Am. Chem. Soc. **54**, 2850 (1932).
[3] Onnes and Crommelin, Leiden Comm. 137a (1913).

II. APPARATUS AND METHOD OF MEASUREMENT

The apparatus used is shown diagrammatically in figure 1. Electrolytic hydrogen of high purity, containing less than 0.02 mole percent of air, from cylinder *A* was passed over copper gauze in tube *B* at 600° C to remove oxygen and insure the normal concentration of the ortho and para varieties. It then passed through a cotton filter in the U-tube *C*, which was surrounded by liquid air, to remove water vapor. When measurements were to be made on normal hydrogen, the hydrogen was then allowed to pass through stopcocks 1 and 2 directly to the calibrated fused-quartz dilatometer *D*, of about 3-cm³ capacity, Parahydrogen was obtained by condensing hydrogen in the U-tube *E* containing zinc chromite, an ortho-para conversion catalyst.[4 5] After allowing it to stand in contact with the catalyst at liquid-hydrogen temperatures 1½ to 4 hours, for complete conversion, the parahydrogen was transferred into the dilatometer by opening stopcocks 3 and 2 and reducing the pressure above the hydrogen bath *H* by means of a vacuum pump. The molecular volume obtained for parahydrogen was the same whether the hydrogen had been in contact with the catalyst 1½ or 4 hours, indicating that the conversion to the low-temperature equilibrium concentration was complete.

In order to determine the temperature of the liquid-hydrogen bath surrounding the dilatometer, normal hydrogen was condensed in the tube *J* and its vapor pressure was read on manometer *F*. An electrical heater at the bottom of the liquid-hydrogen bath caused boiling and promoted uniformity of temperature.[6] The volume of the condensed hydrogen was determined by reading the position of the liquid meniscus in the tube of the dilatometer by means of a scale fastened to the tube. The flasks surrounding the dilatometer were unsilvered. Reference marks on the fused-quartz dilatometer tube provided a means of determining the length of the scale at liquid-hydrogen temperature. The volume of the liquid was measured at several temperatures, obtained by adjusting the pressure over the liquid-hydrogen bath.

The amount of hydrogen used was determined from measurements of the pressure and temperature of the gas in a flask of known volume. After the measurements of the volume of the liquid in the dilatometer were completed stopcock 4 was opened and the hydrogen allowed to evaporate into flask *G*. The tube *J* and manometer *F* were evacuated and the whole apparatus allowed to warm up to room temperature overnight. The next day the pressure of the hydrogen in flask *G* was measured with the manometer *F*. The flask was surrounded by a stirred, insulated water bath at approximately room temperature. A careful determination of the volume of the flask and connecting tubes was made after all other measurements were completed. The volume outside the water bath was only about 18 cm³, the volume of the flask *G* being 3,264 cm³. The volume of the hydrogen at 0° C and 1 atmosphere was computed from readings of the pressure in the flask *G*

[4] H. Diamond, Thesis, Princeton University (1935).
[5] Brickwedde, Scott, and Taylor, J. Research NBS **15**, 463 (1935), RP841; J. Chem. Phys. **3**, 653 (1935).
[6] In order to be certain that the heater did not raise the temperature of the bulb above that of the bath, a number of volume determinations were made with the heater current turned off during the readings. No difference was observed. However, if the heater was not used at all, superheating of the bath caused random scattering of the results.

at the temperature of the water bath, using the P-V-T relations for hydrogen given in the International Critical Tables.[7] A small correction, about 0.2 cm^3, was necessary to compensate for the change in volume of the flask with pressure, since the amount of hydrogen used produced a pressure of about 630 mm of Hg instead of 1 atmosphere.

The expansion of the fused-quartz dilatometer between 20° C and liquid-hydrogen temperature was taken as 0.000165, which is the mean of some unpublished measurements of this laboratory on three different specimens of fused quartz. A correction had to be made for the hydrogen vapor above the liquid in the capillary tube of the dilatometer. The part of this correction which arises from that section of the tube (0.75-mm bore) extending from the top of the liquid-hydrogen bath to the part at room temperature was somewhat uncertain since the temperature along the tube was estimated. However, the correction for this intermediate section amounted to only about 0.012 percent of the final result.

The readings on the vapor pressure of normal hydrogen, from which the temperatures were calculated, were corrected for the uncatalyzed ortho to para conversion of liquid hydrogen, in accordance with measurements made previously of the change in the vapor pressure of hydrogen with time.[8] After the limiting volume of parahydrogen had been determined, a similar correction was made for the change in volume of liquid normal hydrogen with time, which also results from the uncatalyzed ortho to para conversion.

III. RESULTS

The molecular volume of the liquid was calculated from the experimentally determined ratios of the volume of the gas to the volume of the liquid, V_{gas}/V_{liq}, using 22,428 cm^3 $mole^{-1}$ as the molecular volume of hydrogen at 0° C and 1 normal atmosphere. This value for the molecular volume of hydrogen was computed from the volume of an ideal gas, 22,414 cm^3 $mole^{-1}$ [9], at the same temperature and pressure and the value [10] 0.99939 for $1+\lambda$, defined by the equation

$$1+\lambda=\frac{p_0V_0(0°C,\ 0\ atm)}{p_1V_1(0°C,\ 1\ A_n)}$$

Table 1 contains the results of the measurements on normal hydrogen. The temperatures given in column 3 were calculated from the corresponding corrected vapor pressures of normal hydrogen, column 2, by means of the following vapor-pressure equation, used in previous papers:

$$\log_{10}P(\text{mm of Hg})=4.6633-\frac{44.7291}{T}+0.02023T \qquad (1)$$

It was found that the volume-temperature relations of liquid normal hydrogen and liquid parahydrogen at their respective saturation pressures could be represented by a quadratic equation of the form:

$$V=A+BT+CT^2 \qquad (2)$$

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[7] 3, 4 (1928).
[8] Scott, Brickwedde, Urey, and Wahl, J. Chem. Phys. 2, 458 (1934).
[9] Birge, Phys. Rev. Supp. 1, no. 1 (1929).
[10] International Critical Tables 3, 3 (1928).

TABLE 1.—*Molecular volume of liquid normal hydrogen at saturation pressure (experimental data)*

Date (1936)	P (n-H_2)[a]	T	V_{gas}/V_{liq}[a] (Observed)	V_{liq}(obs)	ΔV_{liq} (obs−calc)
	mm of Hg	°K		cm³ mole⁻¹	cm³ mole⁻¹
July 15	749.8	20.34	789.87	28.395	+0.015
15	65.0	14.25	856.71	26.179	−.009
23	754.1	20.35	790.10	28.386	+.002
23	65.4	14.26	855.79	26.207	+.016
23	220.0	16.81	830.67	27.000	+.005
23	335.3	17.89	819.04	27.383	−.002
23	518.8	19.15	804.75	27.870	−.007
23	751.4	20.34	790.00	28.300	+.010
30	752.4	20.35	790.03	28.389	+.005
30	81.7	14.67	852.36	26.313	+.004
30	108.7	15.24	846.72	26.488	+.008
30	201.8	16.60	832.87	26.930	+.008
30	308.9	17.67	821.30	27.308	+.005
30	410.2	18.46	812.79	27.594	−.009
30	571.8	19.45	800.73	28.009	+.009
30	751.7	20.34	790.08	28.387	+.007
August 7	758.7	20.37	790.20	28.383	−.010
7	79.5	14.62	853.30	26.284	−.011
7	111.2	15.29	846.59	26.492	−.004
7	186.7	16.42	834.94	26.862	+.001
7	290.7	17.51	823.38	27.239	−.005
7	450.6	18.73	809.78	27.696	−.013
7	550.9	19.34	802.64	27.943	−.012
7	756.9	20.37	790.23	28.382	−.010

[a] Corrected for the uncatalyzed ortho to para conversion of liquid hydrogen.

The values of the constants A, B and C for liquid normal hydrogen, calculated from the data by the method of least squares, were found to be:

$$A=24.747$$
$$B=-0.08005$$
$$C=0.012716$$

Column 6, table 1, shows the difference between the observed and calculated volumes of liquid normal hydrogen.

Table 2 shows corresponding results on parahydrogen. The values of the constants in eq 2 representing the molecular volume-temperature relation of liquid parahydrogen, also calculated by the method of least squares, are:

$$A=24.902$$
$$B=-0.0888$$
$$C=0.013104$$

Table 3 gives the molecular volume and expansivity $1/V_{20.38}\,(dV/dT)$ at saturation pressure of normal and parahydrogen, calculated from eq 2. The densities of n-H_2 and p-H_2 (table 3) were calculated from the molecular volumes and the molecular weight of H_2. The molecular weight of hydrogen containing the normal amount (D/H = 1/6500) of deuterium is 2.0161 g.[11] The molecular weight of pure protium hydrogen (H_2^1) is 2.0158 so that the densities of liquid protium hydrogen are 3 parts in 20,000 less than the densities of naturally occurring hydrogen.

[11] The atomic weight of naturally occurring hydrogen (1.00805) used in this paper is based on the mass spectrograph results of Aston and Bainbridge, and the latest values of the relative abundances of the isotopes of hydrogen and oxygen. See F. W. Aston, Nature **137**°, 357 (1936); K. T. Bainbridge and E. B. Jordan, Bul. Amer. Phys. Soc. **11**, 18 (1936); Manian, Urey, and Bleakney, J. Am. Chem. Soc. **56**, 2601 (1936); N. T. Hall and T. O. Jones, J. Am. Chem. Soc. **56**, 1915 (1936). The value used for the abundance of O^{17}:O^{16} = 0.0004:1.

TABLE 2.—*Molecular volume of liquid parahydrogen at saturation pressure (experimental data)*

Date (1936)	$P(n\text{-}H_2)$[a]	T	V_{gas}/V_{liq} (observed)	V_{liq}(obs)	ΔV_{liq} (obs−cal.)
	mm of Hg	°K		cm³ mole⁻¹	cm³ mole⁻¹
August 27	68.5	14.35	851.82	26.330	+0.004
27	117.9	15.41	841.62	26.649	+.004
27	221.8	16.83	826.97	27.121	+.002
27	374.0	18.19	811.86	27.625	+.002
27	633.7	19.78	793.44	28.267	−.005
27	754.2	20.36	786.16	28.529	+.003
28	140.5	15.78	838.33	26.753	−.000
28	314.7	17.72	817.08	27.449	+.006
28	567.8	19.43	797.56	28.121	−.003
28	748.3	20.33	786.57	28.514	−.003

[a] Corrected for the uncatalyzed ortho to para conversion of liquid hydrogen.

TABLE 3.—*Molecular volumes, coefficients of expansion, and densities of liquid normal and parahydrogen at saturation pressure*

T	Normal hydrogen			Parahydrogen			Difference (para-normal)	
	V	$\frac{1}{V_{20.38°K}}\frac{dV}{dT}$	ρ	V	$\frac{1}{V_{20.38°K}}\frac{dV}{dT}$	ρ	ΔV	$\Delta\frac{1}{V_{20.38°K}}\frac{dV}{dT}$
°K	cm³ mole⁻¹	°K⁻¹	g cm⁻³	cm³ mole⁻¹	°K⁻¹	g cm⁻³	cm³ mole⁻¹	°K⁻¹
20.38	28.397	0.01543	0.07099	28.535	0.01561	0.07065	0.138	0.00018
20.00	28.232	.01509	.07141	28.368	.01526	.07107	.136	.00017
19.00	27.816	.01420	.07248	27.945	.01434	.07214	.129	.00014
18.00	27.426	.01330	.07351	27.549	.01342	.07318	.123	.00012
17.00	27.061	.01241	.07450	27.179	.01250	.07417	.118	.00009
16.00	26.721	.01151	.07545	26.836	.01158	.07512	.115	.00007
15.00	26.407	.01062	.07634	26.518	.01066	.07602	.112	.00004
14.00	26.119	.00972	.07719	26.227	.00975	.07687	.108	.00003

Column 8 shows the difference in molecular volumes of para and normal hydrogen. It is seen that at the normal boiling point of normal hydrogen the molecular volume of parahydrogen is about 0.138 cm³ mole⁻¹, or 0.49 percent greater than that of normal hydrogen. The values given in column 9 are the differences in expansivities of para and normal hydrogen. The error in these differences in expansivities may be large since their values represent a small difference of two derivatives. They are to be regarded only as indicating the direction and order of magnitude of this difference. The difference in density of normal and parahydrogen is almost constant (column 4−column 7). At 20.38° K this difference is 0.00034 g cm⁻³ and at 14.00° K it is 0.00032 g cm⁻³. The change 0.00002 g cm⁻³ is of the order of magnitude of the probable error of the results.

In estimating the probable error of the results, the deviations of the observed volumes from eq 2 were taken as a measure of that part of the probable error due to accidental errors of observation. This was estimated at ±0.02 percent, somewhat less than the mean deviation of the observations. In addition, systematic errors of measurement were considered. The sources of these systematic errors and their probable magnitudes follow.

1. An error in the determination of the volume of that part of the apparatus in which the amounts of gas were measured: 0.01 percent.

2. An error in the determination of the amount of vapor above the liquid in the dilatometer: 0.01 percent.

3. An error in the correction of the liquid volume and vapor pressure of normal hydrogen for the uncatalyzed ortho to para conversion: 0.01 percent.

4. An error in the determination of the volume of the dilatometer: 0.005 percent.

5. An error caused by a nitrogen impurity in the hydrogen used: 0.0008 percent.

Considering all of the accidental and systematic errors, the probable error of the results is found to be about ± 0.03 percent. The molecular volumes of liquid normal and parahydrogen *at the normal boiling point of normal hydrogen* (20.38° K, according to eq 1) may then be given as:

$$V(n\text{-}H_2) = 28.397 \pm 0.010 \text{ cm}^3 \text{ mole}^{-1}.$$

$$V(p\text{-}H_2) = 28.535 \pm 0.010 \text{ cm}^3 \text{ mole}^{-1}.$$

The difference between the molecular volumes of para and normal hydrogen, while it is not affected by systematic errors of measurement, includes the accidental errors of two different sets of observations, hence the probable error in the difference is also about ± 0.010 cm^3 mole^{-1}. Accordingly, the difference in the molecular volumes of p-H_2 and n-H_2 at the normal boiling point of normal hydrogen is given as

$$\Delta V(p\text{-}H_2) - n\text{-}H_2 = 0.138 \pm 0.010 \text{ cm}^3 \text{ mole}^{-1}.$$

In table 4 the results of our measurements of the molecular volume of liquid normal hydrogen are compared with values calculated from the density of liquid hydrogen as reported by other investigators. Dewar's [12] value is much the highest. He measured the volume of gaseous hydrogen in a bell-jar gas holder. It is possible that errors in the measurement of volume and temperature of the gas resulted in his high value.

Onnes and Crommelin [13] made careful measurements, and the difference between their value and that reported in this paper is too great to be accounted for by ordinary errors of observation. The existence of ortho and para varieties of hydrogen was not known at that time and it is probable that their sample of hydrogen contained an excess of parahydrogen. Evidence to this effect is the fact that their value lies between the values reported here for normal and para hydrogen and is somewhat closer to that for normal hydrogen. Although the method of preparation of their hydrogen is not described in the paper [14] on the density, an earlier communication [15] describes a method of preparation of pure hydrogen by means of two distillations of liquid hydrogen, the hydrogen thus obtained to be used "for the replenishment of thermometers and piezometers." This method would result in a high concentration of parahydrogen, both because of the ortho to para conversion with time and the fractional separation upon distillation. The measurements of Onnes and Crommelin were made over a range of temperatures, making it possible to calculate coefficients of expansion from their data. At the normal boiling point of normal hydrogen the coefficient of expansion determined from their data is 0.0157 (°C)$^{-1}$ as compared with our value of 0.0154 (°C)$^{-1}$.

[12] Dewar. Proc. Roy. Soc. [A] 73, 251 (1904).
[13] Onnes and Crommelin, Leiden Comm. 137a (1937).
[14] See footnote 13.
[15] Onnes, Leiden Comm. 94c, p. 59 (1905).

Augustin [16] gives the density of liquid hydrogen boiling at a pressure of 745.5 mm of Hg as 0.07105 g cm^{-3}. Allowing for expansion, this becomes 0.07097 g cm^{-3} at the normal boiling point of normal hydrogen. Augustin's value agrees very well with ours, but this agreement is probably fortuitous since his individual determinations, four in number, range as much as 0.00013 g cm^{-3} above and below the mean value reported.

TABLE 4.—*Comparison of results of different observers at the normal boiling point of normal hydrogen*

Observer	Date	Method used	Density of liquid n-H_2	Molecular volume of liquid n-H_2
			g cm^{-3}	cm^3 $mole^{-1}$
Dewar	1904	Comparison of volumes of liquid and gas	0.07002	28.79
Onnes and Crommelin	1913	do	.07086	28.45
Augustin	1914	Weighing a sinker in liquid hydrogen	.07097	28.41
Scott and Brickwedde	1937	Comparison of volumes of liquid and gas	.07099	28.397

IV. THEORETICAL CONSIDERATIONS

As was pointed out in section I, the sign of the difference in the lattice energies and molecular volumes of the rotating and nonrotating varieties of H_2 in a condensed phase is opposite to the sign of the change observed in other substances when passing through the transition from the state of molecular orientation to the state of molecular rotation. The Heisenberg Uncertainty Principle, when applied to the problem of a nonrotating molecule oscillating about a direction of molecular orientation ($\Delta\theta \cdot \Delta[I\dot{\theta}] \sim h$), shows that for large amplitudes of oscillation, up to 90°, the zero-point energy of the oscillatory motion is of the order of the energy of the rotational level $j=1$, and for smaller amplitudes the zero-point energy is even larger. Because of the small moment of inertia of the H_2 molecule this zero-point energy for an oscillatory motion of p-H_2 molecules would be large, of the order of 300 cal or more. The Raman spectrum of hydrogen arising from transitions between rotational levels is the same for the gaseous and liquid phases [17] to within the accuracy of the measurements showing that the rotational states are characterized by practically the same energy differences in the gaseous and liquid states. This makes it appear unlikely that liquid p-H_2 could have a large zero-point oscillatory energy, and hence, the directions of orientation of the axes of the nonrotating p-H_2 molecules in both the liquid and solid phases must be randomly distributed. In this respect of randomness of orientation of the axes of molecules, the state of nonrotating p-H_2 is like that at high temperatures in other substances whose molecules are rotating, since for large rotational quantum numbers the distribution of the axes of the rotating molecules is practically uniform.

The axes of rotation of the o-H_2 molecules in the liquid and solid phases are oriented. At temperatures below the critical point of hydrogen (33° K), practically all o-H_2 molecules are in the state $j=1$,

[16] Augustin, Ann. Phys. 46, 419 (1915).
[17] J. C. McLennan and J. H. McLeod, Roy. Soc. Canada, Trans. 23, section 3, 19-20 (1929).

and the three possible orientations of the axis of rotation of an o-H_2 molecule in liquid or solid hydrogen are characterized by the quantum numbers $m=0,\pm1$. At 0° K all the o-H_2 molecules are concentrated in the state of orientation (m state) having the lowest energy, and in the temperature range below 12° K, in which the specific heat of solid o-H_2 exceeds that of solid p-H_2,[18] molecules are being raised to the m states of higher energy. In the liquid and solid phases, the orientations of the axes of the o-H_2 molecules are not randomly distributed in all possible directions as in the case of p-H_2, hence o-H_2 corresponds more nearly with other substances at low temperatures where their molecules are oriented and do not rotate, than with these substances at high temperatures where the molecules rotate.

The difference in molecular volumes of the condensed phases of o- and p-H_2 arises from a difference in the intermolecular forces. To the difference in intermolecular forces must also be attributed the difference in "lattice" energies responsible for the differences in vapor pressures of the ortho and para varieties. It is expected that the Van der Waals attractive forces will be very nearly the same for o- and p-H_2 since these forces arising from "orbital" electron resonance in neighboring molecules are not appreciably influenced by molecular rotation. However, the intermolecular forces of repulsion, which arise from the repulsion of regions of high electron density in neighboring molecules, must be different for o- and p-H_2 since their distributions of electron charge density are different. It is then this difference in the distribution of the average electron-charge density that is responsible for the differences in molecular volume and vapor pressure.

Not only is there a difference in the magnitude of the intermolecular forces of o- and p-H_2, but there is also a difference in the symmetry, that is dependence on the angle, of the forces. In liquid and solid o-H_2 the axes of rotation of the o-H_2 molecules are oriented. The forces of molecular orientation in o-H_2 arise from the nonspherical character of the average electron density of the rotating hydrogen molecule. The dependence of the electron density on the polar angle for the rotational state characterized by the quantum numbers j, m, is given by the square of the associated Legendre polymonial $P_{j,\,m}(\cos\theta)$, which expresses the dependence on θ of the ψ-function for the diatomic rotator.[19] For p-H_2, $j, m=0$, 0, $(P_{0,\,0})^2=1$; for o-H_2, $j, m=1$, 0, $(P_{1,\,0})^2=\cos^2\theta$ and for o-H_2, $j, m=\pm1$, $(P_{1,\,1})^2=\sin^2\theta$. Thus the electron distribution of p-H_2 at low temperatures is spherically symmetrical and no forces of orientation arise. For the o-H_2 state of lowest energy, $j, m=1$, 0, the electron distribution is densest along the polar axis, whereas for the states, j, $m=1, \pm1$ it is densest over the equatorial plane. It is to be expected, therefore, that as the population of the three m states of o-H_2 changes, the forces of orientation will also change.

The average electron distribution for the three m states of o-H_2 ($j=1$) is uniform over all directions as is seen by normalizing the ψ-functions for the three m states and adding. Therefore, above about 12° K the average electron distribution of all the o-H_2 molecules is uniform like that characteristic of p-H_2 ($j=o$). At any instant,

[18] Simon, Mendelssohn, and Ruhemann, Z. physik. Chem. [B] **15**, 121 (1931). Also A. Farkas, Orthohydrogen, Parahydrogen, and Heavy Hydrogen, Cambridge University Press, p. 35-37 (1935).

[19] See Ruark and Urey, Atoms, Molecules, and Quanta, p. 527-531, McGraw-Hill Book Co., New York, N. Y. (1930); A. Farkas, Orthohydrogen, Parahydrogen, and Heavy Hydrogen, p. 35-37, Cambridge University Press, (1935).

however, an individual o-H_2 molecule is in only one of the three m states so that its electron distribution is not uniform but is that characteristic of its quantum number m at that instant. Even at temperatures above 12° K, then, there is a difference between the electron distributions of the individual ortho and para molecules. It is to this nonuniform electron distribution of the individual o-H_2 molecules that is attributed the differences between the intermolecular forces and properties of the condensed states of o- and p-H_2 above 12° K.

From the difference between the specific heats of solids o- and p-H_2, it is possible to determine the magnitude of the force of orientation in solid o-H_2. In an o-H_2 crystal whose molecules are all in the state, j, $m=1$, 0 the molecules will orient themselves so that their angular velocity vectors are aligned perpendicular to the principal axis of the hexagonal crystal. The potential of the orienting force may be represented to a first approximation by equation $V=V_0(1-\cos 2\theta)$ $=2V_0 \sin^2\theta$. In the presence of a force of molecular orientation given by this equation the energies of the states, j, $m=1,\pm 1$ are greater[20] than the energy of the state, j, $m=1,0$ by $4/5)V_0$. The value of V_0 calculated from the difference between the specific heat of solid 100-percent p-H_2 and the specific heat of solid mixtures of o- and p-H_2[21] at 7° K is about 14 cal mole $^{-1}$. The value of V_0 calculated from the difference in specific heats at higher temperatures is smaller (9 cal mole^{-1} at 10° K). This difference is in agreement with a change expected in the forces of molecular orientation as the population of the three m states changes.

It seems probable that the mutual repulsion of regions of high electron density will permit a closer packing of o-H_2 molecules with high electron density along a line ($m=0$), than o-H_2 molecules with high density over a plane ($m=\pm 1$). This makes the o-H_2 state j, $m=1,0$ the low energy state of o-H_2 stable at $0°K$ as was assumed in the preceding paragraph rather than either of the states $j,m=1,\pm 1$. The specific-heat data are in accord with this, as will now be shown. The angular velocity vectors of the molecules in a crystal of o-H_2 all in the states, $j,m=1,\pm 1$ would be directed along the principal axis of the hexagonal crystals so that the potential of the orienting force could be represented to a first approximation by the equation $V=V_0$ $(1+\cos 2\theta)=2V_0\cos^2\theta$. For this case we find that the energy of the state $j,m=1,0$ is greater than that of the states $j,m=1,\pm 1$ by $(4/5)V_0$, which leads to a maximum value of 0.48 cal °K^{-1} (mole of o-H_2)$^{-1}$ for the difference between the specific heats of solid p-H_2 and a solid solution of o-H_2 and p-H_2 assuming V_0 is independent of the temperature. The experimentally measured specific heat of a solid solution containing 50 percent of o-H_2 exceeds that of solid p-H_2 at 5° K by 0.79 cal °K^{-1} (mole of o-H_2)$^{-1}$ and at this temperature, the lowest reached in the calorimetric experiments, the difference is increasing toward lower temperatures. It seems more reasonable that the low-energy state of o-H_2 is the state $j,m=1,0$, than that this difference in specific heats is to be attributed to the rapid rate of decrease of V_0 with temperature (larger than 8 cal °K^{-1} (mole of o-H_2)$^{-1}$) needed to account for it if the low-energy state is $m=+1$ or -1.

It is customary to represent graphically the intermolecular forces in a condensed phase by the "lattice potential-energy curve" and to

[20] Scott, Brickwedde, Urey, and Wahl, J. Chem. Phys. 2; 458 (1934).
[21] See footnote 18.

use this curve in demonstrating in a qualitative manner properties of the condensed phase. If the Van der Waals attractive forces are very nearly the same for *o*- and *p*-H_2, the potential-energy curves of the ortho and para varieties coincide at large values of the distance between the molecules (fig. 2). The repulsive forces are different for *o*- and *p*-H_2 and the two curves deviate from each other at small intermolecular separations. The nearly equal expansivities and specific heats above 12° K of solid and liquid *o*- and *p*-H_2 are in accord with the similar shapes of the two curves. Actually, the expansivity of *p*-H_2 is slightly larger than that of *o*-H_2, and this difference is in the direction to be accounted for by the two curves as represented in figure 2.

At 0° K, at which temperature the *o*-H_2 molecules are concentrated in the state $m=0$, it is probable that the force of orientation is most

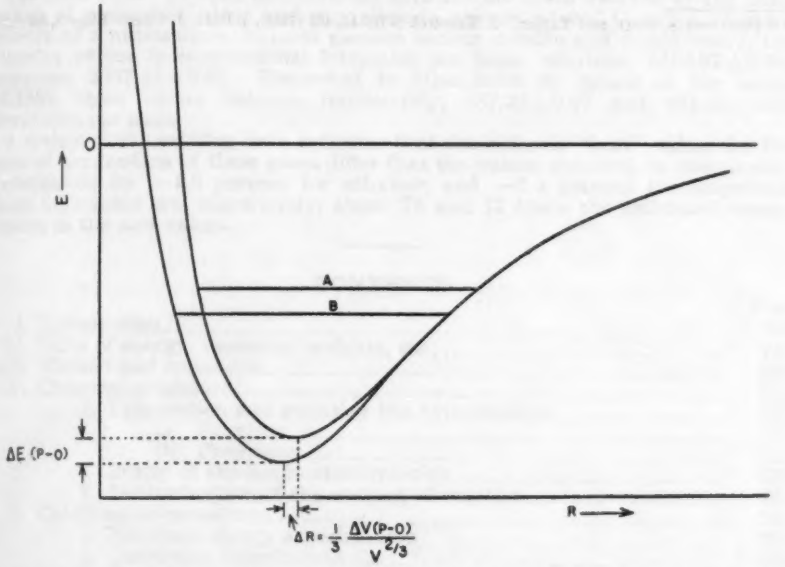

FIGURE 2.—*Diagram illustrating the relation of the "lattice potential-energy curves" of p- and o-H_2 in which the lattice potential energy E is represented as a function of the intermolecular distance R as abscissa.*

Horizontal lines *A* and *B* represent the lattice energies, kinetic and potential, of *p*- and *o*-H_2 at some temperature, the same for both *p*- and *o*-H_2. This figure is not drawn to scale.

intense and the difference in molecular volume of the ortho and para varieties is largest. In the temperature range in which the population of the states $m=\pm 1$ is changing rapidly, the difference in molecular volumes and the relative positions of the potential-energy curves will change most rapidly. As the temperature is raised above 12° K, the increasing thermal agitation will interfere to a greater and greater extent with the alignment of the *o*-H_2 molecules, and the potential-energy curve of *o*-H_2 will move towards that of *p*-H_2. For solutions of *o*-H_2 and *p*-H_2, the average potential-energy curve will lie between those of its pure constituents, its exact position and the forces of orientation depending upon the concentration.

It was shown in a previous paper [22] that the vapor pressure of the nonrotating o-D_2 is greater than that of the rotating p-D_2 and in this respect o-D_2 corresponds to p-H_2. It was further demonstrated that the ortho-para vapor-pressure difference of D_2 is comparable in magnitude with that of H_2. Hence it is expected that there is a difference in the molecular volumes of o-D_2 and p-D_2 comparable in magnitude with the difference in molecular volumes of p-H_2 and o-H_2, the molecular volume of o-D_2 being greater than that of p-D_2.

The authors thank Prof. Edward Teller for the opportunity of discussing the results of this experiment with him and for the helpful suggestions he made.

WASHINGTON, May 27, 1937.

[22] Brickwedde, Scott, and Taylor. J. Research NBS 15, 463 (1935), RP841; J. Chem. Phys. 3, 653 (1935)

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CALORIMETRIC DETERMINATION OF THE HEATS OF COMBUSTION OF ETHYLENE AND PROPYLENE

By Frederick D. Rossini and John W. Knowlton

ABSTRACT

The data of the present investigation give for the heats evolved in the combustion of gaseous ethylene and propylene in oxygen, at 25° C and a constant pressure of 1 atmosphere, to form gaseous carbon dioxide and liquid water, the following values in international kilojoules per mole: ethylene, 1410.97 ± 0.30; propylene, 2057.42 ± 0.62. Converted to kilocalories by means of the factor 1/4.1833, these values become, respectively, 337.28 ± 0.07 and 491.82 ± 0.15 kilocalories per mole.

A review of the existing data indicates that the hitherto "best" values for the heats of combustion of these gases differ fron the values obtained in the present investigation by −1.6 percent for ethylene and −0.4 percent for propylene. These differences are, respectively, about 75 and 12 times the estimated uncertainties in the new values.

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I. INTRODUCTION

Ethylene and propylene are two hydrocarbon gases which have become very important within recent years, because of their availability (of the order of 100,000,000,000 cubic feet annually) as by-products from the "cracking" processes of the petroleum industry, and because of their use in the synthesis of alcohols and other chemical substances, as well as of synthetic motor fuels with superior properties. If such processes are to be carried on with an economy of time, energy, and material, it is important that there be accurately known the thermodynamic properties of the reactants and products of these reactions.

The last determination of the heat of combustion of ethylene was reported in 1901, and that for propylene in 1893. Since those determinations were made, the accuracy of calorimetric measurements has been greatly improved, and it has become possible to obtain these gases in a substantially pure state. Because the old value for the heat of combustion of ethane was found to be in error by about 1 percent [1],[1] it was suspected that the present "best" values for ethylene and propylene might also be in considerable error. For these reasons, it was desirable that new determinations be made of the heats of combustion of ethylene and propylene.

Furthermore, new values for these gases can be used to deduce reliable values for the heats of combustion and formation of all the gaseous normal olefin (alkene-1) hydrocarbons, by making use of the following: 1, the generalization recently made by Rossini [2] that, in any organic molecule containing a normal alkyl group of more than five carbon atoms, the addition of a CH_2 group to the normal alkyl group to form the next higher normal alkyl group results in an increase in the heat of combustion of the organic molecule in the gaseous state, at 25° C and a constant pressure of 1 atmosphere, of 157.00 ± 0.08 kilocalories per mole; 2, the data on the heats of combustion of the gaseous normal paraffin hydrocarbons obtained in this laboratory [1, 2]; and 3, the data on the heats of hydrogenation of some olefin-1 hydrocarbons recently reported by Kistiakowsky, Vaughan, and their coworkers [3, 4].

II. UNITS OF ENERGY, MOLECULAR WEIGHTS, ETC.

The unit of energy employed in this work is the international joule, based upon standards of electromotive force and resistance maintained at this Bureau. In order to report the results in calories, as well as in the fundamental unit of electrical energy, values in international joules are converted to a conventional, defined calorie by means of the selected factor 1/4.1833. This is the same factor that is being used in practically all the laboratories in this country and which has been used in previous conversions of values from this laboratory [5].

As in the previous work on the hydrocarbons, *the thermal data obtained are independent of the atomic weight of carbon*, 1 mole of ethylene being taken as equivalent to 2(18.0156) g of water formed in the combustion and 1 mole of propylene to 3(18.0156) g [5]. In reducing the data of the analytical combustion experiments, the molecular weight of CO_2 was taken to be 44.010 [12].

III. METHOD AND APPARATUS

The calorimetric method employed in the present investigation has been described previously [6, 5]. It has already been pointed out that in the "substitution" method of measuring heats of chemical reactions, neither the size of a degree of temperature nor the true heat capacity of the calorimeter system need be known.[2] In order to emphasize further the substitutional nature of the calorimetric determinations, wherein the heat evolved by a measured amount of chemical reaction is compared with the heat evolved by a measured amount of electrical energy, using the calorimeter as the absorber and comparator of the two kinds of energy, the data on the electrical-energy equivalent of

[1] The numbers in brackets throughout the text refer to the references at the end of this paper.
[2] See p. 11 of reference [6] and p. 243 of reference [5].

the calorimeter are reduced to international joules per ohm increase in resistance of the given platinum resistance thermometer, as determined with the given resistance bridge, at the given mean temperature of the experiments.

Before the beginning of the present investigation, a new platinum resistance thermometer of the regular flat calorimetric type [7, 8] was installed. The constants on this thermometer, no. 262,214, were determined by the Thermometry Section of this Bureau to be as follows: $\delta=1.475$, $R_{0°\,C}=25.5740$, and $R_{100°\,C}=35.5735$, NBS international ohms. For this thermometer, the relation between its resistance, expressed in international ohms, and the temperature in degrees centigrade is as follows:

$$R=25.5740+0.101470t-0.00001475t^2 \text{ international ohms};$$
$$dR/dt=0.101470-0.00002950\ t \text{ international ohms degree}^{-1};$$
$$d^2R/dt^2=-0.00002950 \text{ international ohms degree}^{-2}.$$

And in terms of absolute ohms (taking 1 international ohm=1.00046 absolute ohms), the relation is as follows:

$$R=25.5858+0.101517\ t-0.00001476\ t^2 \text{ absolute ohms};$$
$$dR/dt=0.101517-0.00002952\ t \text{ absolute ohms degree}^{-1};$$
$$d^2R/dt^2=-0.00002952 \text{ absolute ohms degree}^{-2}.$$

At the conclusion of the experiments on ethylene, and before the beginning of the experiments on propylene, a new bridge for measuring the resistance of the platinum thermometer was installed. This bridge was designed by E. F. Mueller [9] of this Bureau and made by the Eppley Laboratories, using substantially the electrical circuit described by Eppley [10]. The new bridge has all the coils of large resistance maintained at constant temperature in a metal block, so that the readings are practically independent of the room temperature. The commutator and several adjusting devices are incorporated into the bridge proper. These latter include an adjustable resistance for regulating the current through the bridge circuit so as to obtain a sensitivity on the galvanometer scale of an even number of mm per ohm (in the present assembly, the sensitivity was adjusted to 1 mm per 0.00001 ohm, or about 0.0001° C); an adjustable resistance which can be placed in series or in parallel with the galvanometer in order to obtain proper damping; an extra 0.5-ohm plug which can be used to remove 0.5 ohm from the "known" arm of the bridge, in order that temperature changes of about 6° C or less can always be measured without disturbing the settings on the decade of 1-ohm coils.

During the present investigation, the unsaturated standard cells previously used, in connection with the determination of the electrical power with the White "double" potentiometer, were replaced by two saturated standard cells kept at 30° C in a metal box similar to that described by Mueller and Stimson [15]. These standard cells were calibrated and kindly supplied to us by the Standard Cell Laboratory of this Bureau.

For the present experiments, there was used a new reaction vessel, which was identical with that used for propane, normal butane, normal pentane, and isobutane, and previously described [1], except that the burner tube and injector were altered in size to be suitable for the higher flame velocities of ethylene and propylene.

IV. CHEMICAL PROCEDURE

1. PREPARATION AND PURITY OF THE HYDROCARBONS

(a) ETHYLENE

The sample of ethylene used in the present investigation was prepared to our order by the Linde Air Products Co., Buffalo, N. Y., by the fractional distillation of petroleum products. In our laboratory, the ethylene was examined for impurities by means of Shepherd's differential vapor-pressure apparatus [11], and by determination of the ratio of carbon to hydrogen in the sample [12]. The Linde Air Products Co. reported that this sample of ethylene contained about 0.15 percent of ethane as impurity.

At the suggestion of Martin Shepherd, the differential vapor-pressure measurements were carried out in such a way as to make them quantitative with respect to the amount of impurity in the entire sample. Since practically all of the impurity was less volatile than ethylene itself, it would be concentrated in the last distillation fractions. In several experiments, a 2-ml sample of liquid ethylene was separated by isothermal distillation into an "initial distillate" of 10 percent, a "second cut" of 35 percent, a "middle cut" of 10 percent, and a series of fractions from the "middle cut" to the "residue." The data given in table 1 were obtained in this manner, the "middle cut" being assumed to be pure ethylene. The uncertainties given in the table were estimated from the data. The method of making these calculations has already been described [11].

TABLE 1.—*Data on the determination of the amount of impurity in ethylene by differential vapor-pressure measurements*

Series	Fraction	Mole fraction of impurity in the given fraction	Corresponding mole fraction of impurity in the entire sample	Total amount of the given impurity in the entire sample
	Percent			*Mole fraction*
I	95 to 100	0.0143	0.00072	0.0020±0.0005 (ethane).
	85 to 95	.0089	.00089	
	73 to 85	.0025	.00030	
	55 to 73	(.0008)*	(.00013)	
II	90 to 100	0.0122	.00122	.0022± .0005 (ethane).
	80 to 90	.0054	.00054	
	55 to 80	(.0016)*	(.00040)	
III	0 to 10	.0015	.00015	$.0001_5$± $.0001_0$ (methane).

* These values were estimated by extrapolation from the other values.

Six experiments on the determination of the ratio of carbon to hydrogen in the sample of ethylene gave the following results: average amount of ethylene used per experiment, 0.030 mole; average value of the ratio, moles CO_2/moles H_2O, 0.9986_3; average deviation from the mean, $\pm 0.0001_5$; maximum deviation from the mean, 0.0003_4; "uncertainty", calculated as in [5], $\pm 0.0001_7$.

With the amount of methane impurity taken to be that given by the differential vapor-pressure measurements, namely, $0.0001_5 \pm 0.0001_0$ mole fraction, and with the value of the deviation from unity of the C/H ratio giving the sum of methane plus ethane, the mole fraction of ethane is calculated to be $0.0026_0 \pm 0.0003_2$. With the value for the mole fraction of ethane as determined by the vapor-pressure data taken to be 0.0021 ± 0.0005, and with these values weighted inversely as the squares of their estimated uncertainties, there is

obtained for the mole fraction of ethane the weighted mean value $0.0024_8 \pm 0.0002_7$.

(b) PROPYLENE

The Phillips Petroleum Co., at Bartlesville, Okla., supplied gratis to this laboratory 150 g of propylene prepared in their laboratory by the following steps: preparation of a "concentrate" of propylene by fractional distillation of gases from the petroleum cracking process; bromination of this "concentrate"; separation of the dibromides by distillation; regeneration of propylene from the dibromides with zinc and ethyl alcohol; and fractional distillation of the resulting propylene to yield a product measured to be 99.9 percent pure.

In our laboratory, this propylene was subjected to two successive distillations in a vacuum-jacketed spiral column coated internally with carborundum. This column, designed by Martin Shepard [13], had a linear length of about 55 cm and an actual distillation path along the spiral of about 600 cm. In the first distillation, there were discarded an initial distillate of 5 ml and a final residue of 20 ml, leaving a main body of 135 ml. This latter was subjected to a second distillation, which yielded an initial distillate of 5 ml, a final residue of 15 ml, and a main body of 115 ml. Differential vapor-pressure measurements of the initial distillate and of the final residue against a middle cut of 10 ml (taken at the midpoint of the distillation of the main body) indicated that this initial distillate of 5 ml contained 0.0057 mole fraction of a more volatile impurity and the final residue of 15 ml contained 0.0020 mole fraction of a less volatile impurity. Assuming that the separation obtained with this column was substantially complete, these data would indicate that the entire sample contained, before the second distillation, about 0.0004_3 mole fraction of impurity. The main body from the second distillation would therefore be expected to be substantially pure.

Four experiments on the determination of the ratio of carbon to hydrogen in the sample of propylene gave the following results (see p. 254): average amount of propylene used per experiment, 0.030 mole; average value of the ratio, moles CO_2/moles H_2O, 0.9999_7; average deviation from the mean, $\pm 0.0001_8$; maximum deviation from the mean, 0.0003_0; "uncertainty", calculated as in [5], $\pm 0.0002_4$.

On the basis of the above data, it is concluded that the purity of this sample of propylene was such that, per mole of water formed, the heat of combustion of this sample would differ from that of an absolutely pure sample of propylene by less than 0.01 percent.

2. PURITY OF THE COMBUSTION REACTION

With the combustion reaction proceeding in the calorimetric-reaction vessel, the gaseous products of combustion, for both ethylene and propylene, were examined for the presence of carbon monoxide.[3] No carbon monoxide was found in tests which would have detected an amount corresponding to about 0.00005-mole fraction of the total carbon.

The ethylene was burned in an atmosphere of pure oxygen in the calorimetric-reaction vessel (see fig. 1 of reference [1]), but in the preliminary experiments with propylene it was found that the flame velocity was too great for its proper combustion in this burner. In order to avoid altering the burner, the flame velocity for the propylene combustions was reduced by diluting the oxygen with one-half its

[3] These tests were kindly made by C. Creitz, of the Gas Chemistry Section of this Bureau.

volume of helium (the mixture of oxygen and helium being freed of combustible matter by a preliminary passage through hot copper at 500 to 600° C, and then successively through Ascarite (a mixture of sodium hydroxide and asbestos), anhydrous magnesium perchlorate, and phosphorus pentoxide).

The purity of the ignition process was checked by running a series of ignitions and extinctions of the flame, in order to exaggerate greatly any abnormal effect present, and then comparing the small masses of carbon dioxide and water formed. In the ignitions with ethylene, the masses of carbon dioxide and water balanced, stoichiometrically, within the limits of error of the measurements. In the ignitions with propylene, however, there existed a difference in the increases in mass of the two absorption tubes corresponding to a stoichiometrical deficit of 0.0004_9 g in the carbon dioxide tube, or a surplus of 0.0002_0 g in the water tube, for each ignition operation carried out exactly as in the main analytical experiments. This small correction (amounting to about 0.012 percent) was applied to the data of the experiments on the determination of the carbon-hydrogen ratio (see p. 253). The corresponding correction to the energy of the reaction is discussed on page 256.

3. DETERMINATION OF THE AMOUNT OF REACTION

As in the previous experiments on hydrocarbons [1, 14], the amount of reaction was determined from the mass of water formed in the combustion (see above). One mole (18.0156 g) of water was taken as equivalent to ½ mole of C_2H_4 and to ⅓ mole of C_3H_6, and the resulting values of the heats of combustion are, therefore, independent of the atomic weight of carbon.

V. CALORIMETRIC PROCEDURE

1. ELECTRICAL-ENERGY EXPERIMENTS

The data of the electrical-energy experiments for ethylene are given in table 2, where the various quantities have the same significance as in former reports (see p. 17 of reference [6]), except that the electrical-energy equivalent of the calorimeter system is now expressed in terms of international joules per ohm increase in resistance of the given thermometer as read on the given bridge, the change in resistance being for the given mean temperature of the experiments.

TABLE 2.—*Calorimetric results of the electrical-energy experiments for ethylene*

Experiment	ΔR [1]	k	K	U	Electrical energy [2]	Mass of calorimeter water	Electrical-energy equivalent of calorimeter system [3]	Deviation from mean
	Ohm	min^{-1}	*Ohm*	*Ohm*	*International joules*	g	*International joules/international ohm*	*Joules/ohm*
1	0.412006	0.001948	0.007963	−0.000221	60748.3	3537.97	150767.3	8.3
2	.410889	.001948	.008013	−.000381	60648.5	3543.00	[150686.7]	.....
3	.410894	.001946	.008015	−.000118	60700.3	3546.86	150751.8	−7.1
4	.410133	.001935	.008019	−.000369	60704.4	3551.70	150754.0	−5.0
5	.410749	.001949	.008022	−.000092	60736.6	3550.47	150758.8	−0.2
6	.410181	.001958	.008092	−.000342	60780.9	3547.88	150747.6	−11.4
7	.411637	.001954	.008026	−.000129	60799.6	3545.58	150774.1	15.1
Mean							150759.0	±7.1

[1] The average temperature of the calorimeter was 25.00° C for experiments 3, 4, 5, and 6, and 25.01° C for experiments 1, 2, and 7.

[2] The time of electrical-energy input was 1140.00 seconds in each experiment.

[3] For 3550.00 g of water in the calorimeter and an average temperature of 25.00° C. (See p. 250 regarding the units.)

For the ethylene experiments, thermometer no. 262,214 was used in conjunction with bridge no. 47,669 (Leeds & Northrup), the resistance coils of which are evaluated in international ohms. The "precision uncertainty" [5] of the final value from these experiments is $\pm 0.005_4$ percent.

The data of the electrical-energy experiments for propylene are given in table 3. For these experiments, thermometer no. 262,214 was used in conjunction with bridge no. 404 (Eppley), the resistance coils of which are evaluated in terms of absolute ohms as given by the relation, 1 NBS international ohm = 1.00046 absolute ohms. The "precision uncertainty" [5] of the final value from these experiments is $\pm 0.005_3$ percent.

TABLE 3.—*Calorimetric results of the electrical-energy experiments for propylene*

Experiment	ΔR [1]	k	K	U	Electrical energy [2]	Mass of calorimeter water	Electrical-energy equivalent of calorimeter system [3]	Deviation from mean
	Ohm	min^{-1}	*Ohm*	*Ohm*	*International joules*	*g*	*International joules/absolute ohm*	*Joules/ohm*
1	0.400340	0.001971	0.010689	0.000088	58697.2	3548.58	150733.2	21.4
2	.397638	.001960	.010369	.000289	58144.5	3538.83	150712.7	0.9
3	.396597	.001950	.010654	.000136	58116.2	3548.25	150707.9	−3.9
4	.396470	.001948	.010438	.000184	58041.7	3543.39	150700.2	−11.6
5	.397062	.001968	.010646	.000082	58056.8	3540.91	[150652.2]	
6	.395236	.001947	.010545	.000214	57970.1	3551.30	150723.0	11.2
7	.398970	.001948	.010292	.000143	58598.6	2552.59	150711.9	0.1
8	.399980	.001947	.010353	.000095	58613.3	3544.30	150707.6	−4.2
9	.398560	.001952	.010300	.000116	58462.7	3548.14	150698.1	−13.7
Mean							150711.8	±8.4

[1] The average temperature of the calorimeter was 24.98° C for experiment 6; 24.99° C for experiments 2, 3, 4, 5, and 7; 25.00° C for experiments 8 and 9; and 25.01° C for experiment 1.
[2] The time of electrical-energy input was 1560.00 seconds in each experiment.
[3] For 3550.00 g of water in the calorimeter and an average temperature of 25.00° C. (See p. 250 regarding units.)

2. CORRECTION EXPERIMENTS

The process of ignition and extinction of the flame was checked, as in the previous investigations, by performing a series of ignitions and extinctions of the flame, and making a thermal balance of the sources and sinks of energy, namely the "reaction", "vaporization", "gas", and "spark" energies, each of which was evaluated as before [1].

For a series of seven ignitions and extinctions of the flame with ethylene, carried out under the same conditions as in the main calorimetric combustion experiments, the thermal quantities were out of balance by only 6.4 joules. This corresponds to 0.9 joule for each ignition of the flame, or to about 1 part in 70,000 in the total energy of the main calorimetric combustion experiments. This difference is well within the limits of error of the measurements.

For a series of six ignitions and extinctions of the flame with propylene, it was found that, assuming the increase in mass of the water absorption tube to measure accurately the amount of propylene burned to carbon dioxide and water in these experiments, in which the amount of reaction was very small, the thermal quantities were out of balance by 31.7 joules, which corresponds to a sink of energy of 5.3 joules for each ignition operation carried out exactly as in the

main calorimetric combustion experiments. (This "impurity" in the ignition process for propylene may also be taken care of by assuming a surplus of 0.0001_4 g in the increase in mass of the water absorption tube above that amount representing the true amount of reaction.) Because this small difference was larger than the experimental error of the determination, due account of it was taken by subtracting 5.3 joules from the pure "spark" energy in each main calorimetric combustion experiment to obtain a net "ignition" energy. Since the total magnitude of this correction is about 0.009 percent of the total energy of a main calorimetric combustion experiment, its value needs to be known only to about one-fourth of itself to be entirely without significance in the results. Furthermore, this correction is of the proper sign and magnitude as would be deduced from the direction and amount of the unbalance in the masses of carbon dioxide and water obtained in the ignition operation (see p. 254).

3. REACTION EXPERIMENTS

The data of the reaction experiments for ethylene are given in table 4. The "precision uncertainty" [5] of the final value from these experiments is ± 0.014 percent. The correction for the impurity in the ethylene (see p. 252) is 1.44 ± 0.16 kilojoules per mole.

The data of the reaction experiments for propylene are given in table 5. The "precision uncertainty" [5] of the final value from these experiments is ± 0.028 percent.

TABLE 4.—*Calorimetric results of the reaction experiments for ethylene*

Experiment	ΔR [1]	k	K	U	Electrical-energy equivalent of calorimeter system [2]	"Gas" energy	"Ignition" energy	"Vaporization" energy	Mass of water formed in the reaction	Heat of combustion [3] at 25° C	Deviation from mean
	Ohm	min^{-1}	*Ohm*	*Ohm*	*International joules/international ohm*	*Joules*	*Joules*	*Joules*	g	*International kilojoules/mole*	*Kilojoules/mole*
1	0.403710	0.001964	0.011247	0.000091	150340	16.8	17.1	405.6	1.51728	1411.09	0.12
2	.407606	.001975	.011865	.000087	150143	1.3	10.8	404.9	1.52849	1411.05	.08
3	.407921	.001973	.011321	.000103	150683	1.3	10.8	418.8	1.52997	1411.33	.36
4	.409739	.001966	.012783	.000080	150229	1.6	10.8	399.0	1.53396	1410.99	.02
5	.407826	.001977	.012298	−.000087	150788	−2.5	10.8	373.4	1.53459	1410.65	−.32
6	.408878	.001988	.012314	.000205	150317	−3.0	11.7	370.2	1.53195	1411.24	.27
7	.410182	.001983	.012901	.000099	150720	2.0	13.5	407.6	1.54051	1410.76	−.21
8	.408469	.001979	.012672	.000099	150628	4.0	14.4	415.6	1.53487	[1409.95]	.....
9	.407582	.001986	.013690	.000342	150336	5.6	17.1	418.5	1.52311	1410.63	−.34
Mean	.....	.....	.....	.....	.....	.....	.....	.....	.....	1410.97	±0.22

[1] The average temperature of the calorimeter was 25.00° C for experiments 2, 3, 4, 5, 6, 8, and 9; 24.97° C for experiment 1; and 25.01° C for experiment 7.

[2] Includes the heat capacity of one-half the mass of liquid water formed in the reaction. (See p. 250 regarding units.)

[3] To each value has been added 1.44 kilojoules per mole as a correction for the impurity in the ethylene. (See p. 252.)

TABLE 5.—*Calorimetric results of the reaction experiments for propylene*

Experiment	ΔR [1]	k	K	U	Electrical-energy equivalent of calorimetric system [2]	"Gas" energy	"Ignition" energy	"Vaporization" energy	Mass of water formed in the reaction	Heat of combustion at 25° C	Deviation from mean
	Ohm	min^{-1}	*Ohm*	*Ohm*	*International joules/absolute ohm*	*Joules*	*Joules*	*Joules*	*g*	*International kilojoules/mole*	*Kilojoules/mole*
1	0.398833	0.001967	0.010694	0.000061	150405	0.0	18.7	569.3	1.54783	2057.34	−0.08
2	.399424	.001971	.010005	.000150	150567	0	22.7	481.0	1.55179	2057.31	−.11
3	.399060	.001947	.009625	.000088	150785	0	24.7	496.6	1.55441	2057.67	.25
4	.397818	.001986	.010061	.000377	150440	3.5	18.7	486.5	1.54366	2056.68	−.74
5	.398701	.001961	.010681	.000326	150603	1.7	12.7	555.6	1.54785	2057.63	.21
6	.399116	.001953	.010326	.000058	150628	1.7	10.7	529.8	1.55068	2058.85	1.43
7	.397725	.001964	.010651	.000279	150616	0	12.7	520.0	1.54441	2056.48	−.94
Mean										2057.42	±0.54

[1] The average temperature of the calorimeter was 25.01° C for experiment 1, and 25.00° C for experiments 2, 3, 4, 5, 6, and 7.
[2] Includes the heat capacity of one-half the mass of liquid water formed in the reaction. (See p. 250 regarding units.)

VI. RESULTS OF THE PRESENT INVESTIGATION

The data of the present investigation yield, for the heats of combustion of ethylene and propylene, according to the reaction

$$C_nH_{2n}(g)+3n/2\ O_2(g)=nCO_2(g)+nH_2O\ (liq) \qquad (1)$$

at 25° C and a constant pressure of 1 atmosphere, the values shown in table 6. The uncertainties in the final values were computed as for the previous data [5].

TABLE 6.—*Results of the present investigation*

Reaction: $C_nH_{2n}(g)+3n/2\ O_2(g)=nCO_2(g)+nH_2O(liq)$

Gas	Formula	Heat of combustion $-\Delta H$ at 25° C and 1 atmosphere	
		International kilojoules [1]	*Kilocalories per mole* [2]
Ethylene	C_2H_4	1410.97±0.30	337.28±0.07
Propylene	C_3H_6	2057.42±0.62	491.82±0.15

[1] See p. 250.
[2] See p. 250.

VII. DATA OF PREVIOUS INVESTIGATIONS

1. ETHYLENE

Data on the heat of combustion of ethylene have been reported by Dulong [16], Grassi [17], Favre and Silbermann [18], Andrews [19], Berthelot [20], Berthelot and Matignon [21], Thomsen [22], and Mixter [23]. The first four investigations may now be considered as of historical importance only.

The data of Berthelot and Matignon [21] (see also Berthelot [20]) have already been reviewed (see p. 631 of reference [24]), and yield

for the heat of combustion of ethylene according to reaction (1), at 25° C and 1 atmosphere, $-\Delta H=1426.5\pm6.7$ international kilojoules or 341.0 ± 1.6 kilocalories per mole.

The data of Thomsen [22] have also been reviewed previously (see p. 631 of reference [24]), and yield for the heat of combustion of ethylene according to reaction (1), at 25° C and 1 atmosphere, $-\Delta H=1392.6\pm3.3$ international kilojoules or 332.9 ± 0.8 kilocalories per mole.

Mixter [23] performed three experiments on the combustion of gaseous ethylene (containing several percent of hydrogen) in a bomb at constant volume at about 18° C. In the three experiments the amount of hydrogen present was reported to be 6.3, 2.8, and 3 percent, respectively; and the amount of ethylene, in moles, was deduced from the composition of the gas, the volume of the bomb, and the pressure and temperature at which the bomb was closed. About $\frac{1}{40}$ mole of ethylene was used in each experiment, and the heat evolved was corrected for the combustion of the given amount of hydrogen. With modern values for PV/RT for ethylene at about 18° C and 1 atmosphere,[4] for the heat of combustion of hydrogen, and for the unit of energy [5], there is obtained, from Mixter's data, for the heat evolved in the combustion of ethylene, according to reaction (1) at 25° C and a constant pressure of 1 atmosphere, $-\Delta H=1442\pm10$ international kilojoules or 344.8 ± 2.4 kilocalories per mole. The uncertainty here is calculated according to [5] without taking into account possible systematic errors arising from the calorimetry or chemistry of Mixter's experiments.

It is also possible to calculate a value for the heat of combustion of ethylene from modern values for the heats of combustion of ethane and hydrogen and the heat of hydrogenation of ethylene:

$$C_2H_6(g)+3\tfrac{1}{2}\ O_2(g)=2\ CO_2(g)+3\ H_2O\ (liq) \quad (2)$$

$$H_2(g)+\tfrac{1}{2}\ O_2(g)=H_2O\ (liq) \quad (3)$$

$$C_2H_4(g)+H_2(g)=C_2H_6(g) \quad (4)$$

The sum of reactions (2) and (4) less (3) yields

$$C_2H_4(g)+3\ O_2(g)=2\ CO_2(g)+2\ H_2O\ (liq) \quad (5)$$

With the value of $-\Delta H$ at 25° C and 1 atmosphere for reactions (2) and (3) taken from the previously published data of this laboratory [6, 1] as 1559.57 ±0.44 and 285.775 ±0.040 international kilojoules per mole, respectively, and for reaction (4) from the data of Kistiakowsky, Vaughan, et al. [3, 4, 24] as 136.45 ±0.25 international kilojoules per mole, there is obtained for reaction (5) the value $-\Delta H=1410.25\pm0.52$ international kilojoules or 337.11 ±0.13 kilocalories per mole, at 25° C and 1 atmosphere. The value taken for reaction (4) is the average of the two close values previously deduced [24] from the direct hydrogenation experiments of Kistiakowsky, Vaughan, et al. [3], corrected (+0.022 percent) to the new (44.010) molecular weight of carbon dioxide.

The various experimental values for the heat of combustion of ethylene are shown together in figure 1.

[4] This value was kindly supplied by C. S. Cragoe, of this Bureau.

2. PROPYLENE

Data on the heat of combustion of propylene have been reported by Berthelot [20], Berthelot and Matignon [21], and Thomsen [22].

Berthelot and Matignon [21] (see also Berthelot [20]) performed three experiments on the heat of combustion of propylene in a bomb at constant volume at about 15° C. The amount of reaction was

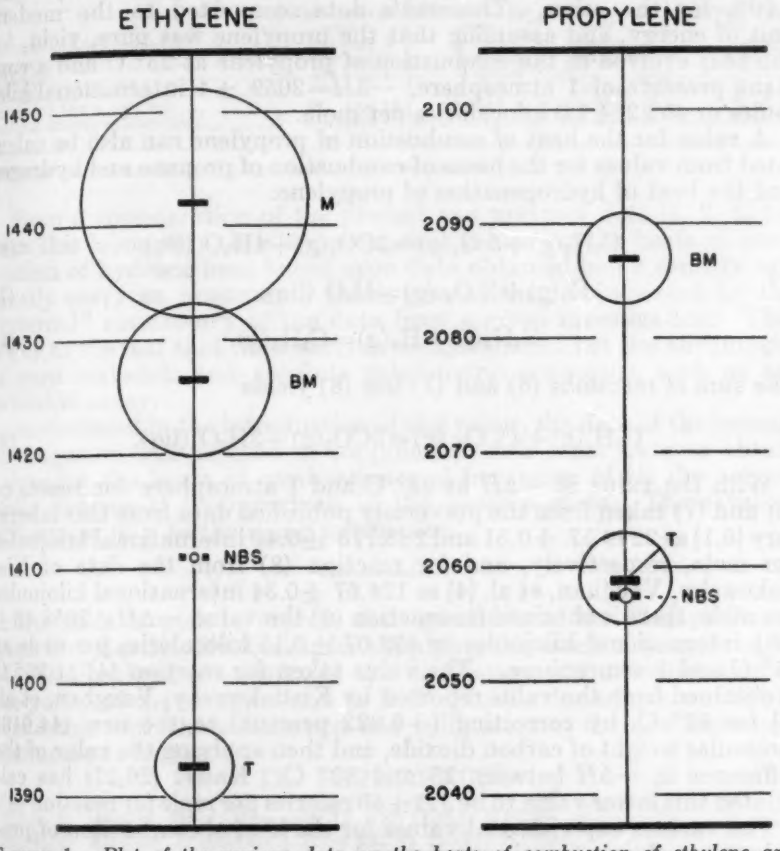

FIGURE 1.—*Plot of the various data on the heats of combustion of ethylene and propylene.*

The scale of ordinates gives the heat of combustion, at 25° C and a constant pressure of 1 atmosphere, in international kilojoules per mole. The average values of each investigation, together with the estimated uncertainties (measured by the radii of the respective circles), are indicated as follows: T, Thomsen [22]; BM, Berthelot and Matignon [21]; M, Mixter [23]; NBS, present investigation.

determined both from the volume of propylene burned and the mass of carbon dioxide formed, though the latter datum was apparently lost for the second experiment. The respective values by the two methods agreed within about 0.1 percent, although no information is given as to the value used for PV/RT for propylene. In terms of the modern unit of energy, these data yield for the heat of combustion of propylene, according to reaction (1) at 25° C and a constant pressure of 1 atmosphere, $-\Delta H=2087 \pm 4$ international kilojoules or 498.9 ± 1.0 kilocalories per mole.

Thomsen [22] performed four experiments on the heat of combustion of propylene in a flame calorimeter at constant pressure and about 18° C, the amount of reaction being determined from the mass of carbon dioxide formed. Thomsen used two different samples of propylene, both prepared chemically, and his values for the ratio of carbon to hydrogen, expressed as the ratio of moles of CO_2 per mole of H_2O, were 0.983_3, 0.991_4, 1.006_7, and 1.002_0 for one sample and 1.005_0 for the other. Thomsen's data, converted to the modern unit of energy, and assuming that the propylene was pure, yield, for the heat evolved in the combustion of propylene at 25° C and a constant pressure of 1 atmosphere, $-\Delta H=2059 \pm 4$ international kilojoules or 492.2 ± 1.0 kilocalories per mole.

A value for the heat of combustion of propylene can also be calculated from values for the heats of combustion of propane and hydrogen and the heat of hydrogenation of propylene:

$$C_3H_8(g)+5\ O_2(g)=3CO_2(g)+4H_2O\ (liq) \quad (6)$$

$$H_2(g)+\tfrac{1}{2}\ O_2\ (g)=H_2O\ (liq) \quad (7)$$

$$C_3H_6(g)+H_2(g)=C_3H_8(g). \quad (8)$$

The sum of reactions (6) and (7) less (8) yields

$$C_3H_6(g)+4\tfrac{1}{2}\ O_2\ (g)=3CO_2(g)+3H_2O\ (liq). \quad (9)$$

With the value of $-\Delta H$ at 25° C and 1 atmosphere for reactions (6) and (7) taken from the previously published data from this laboratory [6,1] as 2219.57 ± 0.51 and 285.775 ± 0.40 international kilojoules per mole, respectively, and for reaction (8) from the data of Kistiakowsky, Vaughan, et al. [4] as 124.67 ± 0.34 international kilojoules per mole, there is obtained for reaction (9) the value $-\Delta H=2058.46 \pm 0.61$ international kilojoules or 492.07 ± 0.15 kilocalories per mole at 25° C and 1 atmosphere. The value taken for reaction (4) at 25° C is obtained from the value reported by Kistiakowsky, Vaughan, et al. [3] for 82° C, by correcting (+0.022 percent) to the new (44.010) molecular weight of carbon dioxide, and then applying the value of the difference in $-\Delta H$ between 25 and 82° C. Kassel [26,27] has calculated this latter value to be 321 ± 40 calories per mole for reaction (8).

The various experimental values for the heat of combustion of propylene are shown together in figure 1.

VIII. CONCLUSION

In table 7 are displayed the various values for the heats of combustion of ethylene and propylene. The values marked ICT [25] are those given in the International Critical Tables as the then "best" values for these thermal constants. The agreement of Thomsen's value for propylene with that from the present investigation appears to be fortuitous. The agreement of the "Calculated" values with those from the present work indicates an accord among the heats of combustion of hydrogen, ethane, and propane, as measured at the National Bureau of Standards [6, 1] and the heats of hydrogenation of ethylene and propylene as measured at Harvard [3, 4].

TABLE 7.—*Values for the heats of combustion of ethylene and of propylene*

Source	Ethylene		Propylene	
	$-\Delta H$ at 25° C and 1 atm	Difference from value of present investigation	$-\Delta H$ at 25° C and 1 atm	Difference from value of present investigation
	Kilocalories per mole [1]	*Kilocalories per mole*	*Kilocalories per mole* [1]	*Kilocalories per mole*
Berthelot and Matignon [21]	341.0±1.6	3.7±1.7	498.9±1.0	7.1±1.2
Thomsen [22]	332.9±0.8	−4.4±0.9	492.2±1.0	0.3±1.2
Mixter [23]	344.8±2.4	7.5±2.5		
ICT [25]	332±?	−5.3±?	490.0±?	−1.8 ±?
Calculated (see p. 258, 260)	337.11±0.13	−0.17±0.20	492.07±0.15	0.25±0.29
National Bureau of Standards	337.28±0.07		491.82±0.15	

[1] Converted from international kilojoules with the factor 1/4.1833.

From a consideration of the present and previous data [1, 2, 6, 14] from this laboratory, it is apparent that values for the heats of combustion of hydrocarbons based upon data obtained half a century ago usually carry an uncertainty much greater than is indicated by the "internal" consistency of the data from a given investigation. This is due to the fact that these early investigators had not the advantages of pure materials and accurate calorimetric apparatus, such as are available today.

As discussed in the introduction of this paper, the data of the present investigation will be used in conjunction with other data to obtain values for the heats of combustion and formation of all the normal olefin (alkene-1) hydrocarbons in the gaseous state. These values will appear in a forthcoming publication.

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RESEARCH PAPER RP1025

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EXTRACTION OF JERUSALEM-ARTICHOKE JUICES IN AN EXPERIMENTAL DIFFUSION BATTERY

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ABSTRACT

In 12 experiments on the extraction of polysaccharides from jerusalem-artichoke tubers, conducted in a column having an average length of 17.75 cells, set up in the miniature diffusion battery described in a previous paper,[1] the mean charge was 1.05 kg of cossettes occupying 51.8 percent of the cell space at a density of filling of 34.6 lb/ft.[3] The volume of the accompanying flood liquid was 915 ml, and the velocity of the flux was 2.85 percent of the column length per minute in a period of 5 minutes, resulting in a rate of extraction of 0.764 g/min/m² of cossette surface calculated as reducing sugars, of which 76.7 percent was levulose. In eight experiments the yield of pulp was 100.5 g/100 g of cossettes and the production of pulp water was 85.4 g/100 g of cossettes. In three experiments the yield of pressed pulp was 45.1 percent, and of dried pulp 4.3 percent of the weight of wet pulp. The polysaccharides containing the higher proportions of levulose apparently diffuse at least as rapidly as those containing smaller proportions of levulose. Attenuation gradients for three columns supply data for a future study of the kinetics of the process.

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I. INTRODUCTION

The present paper is a report on some of the experimental results obtained in the extraction of polysaccharides from cossettes prepared from jerusalem artichokes [2] in the battery previously described.[3] All

[1] J. Research NBS 15, 441 (1935) RP840; Ind. Eng. Chem. 27, 1266 (1935).
[2] J. Research NBS 17, 615 (1936) RP931.
[3] J. Research NBS 15, 441 (1935) RP840; Ind. Eng. Chem. 27, 1266 (1935).

of the experiments, except those relating to reagent dosage, were carried out in the single-row arrangement of the cells, as illustrated in figure 1. Terms defined in either of the previous papers will be used as convenient in the present discussion without further definition.

II. EXPERIMENTAL PROCEDURE

1. SETTING UP THE MATERIAL COLUMN

Generally the battery was started early in the morning. First, the whole battery was heated by filling all of the cells with hot water and then passing hot water fluxwise through the filled cells, while maintaining appropriate pressures of steam on the calorisators. The water was emptied from each cell just previous to the introduction of the cell's first charge of cossettes, and the first charges were usually introduced to the successive cells at intervals of time equal to the charging period,[4] which already had been chosen for the run as a whole. The first cell set-up was primed with hot water, all others with the liquid efflux from the cell next previously set up. In most of the runs the drawing of diffusion juice was begun when about half of the cells in the column were filled; in a few runs, later. Obviously, the first charge from which juice was drawn was the first to receive the full amount of flux for the term of processing. In all previous charges the element of flood recession[5] had been missing from the flux for a duration of from one to several periods. When in addition these charges had been set up more rapidly than the headway selected for the run as a whole, they finally received a total duration of treatment which was less than the standard term of retention for that run. This resulted in somewhat greater rejectment of polysaccharides in the residues for the first round of the battery than for the subsequent rounds in that run.

Once the drawing had been started, the regular periodic procedure was: (1) In most experiments, first to draw from the newly entered charge; then to prime the next charge. In other experiments the procedure was either (2) to prime ahead of drawing, or (3) to draw the last charge and prime the one next to it simultaneously. In the second procedure each charge was left standing in the flooded condition for more than half a period before it was entered into the column; in the first and third procedures it was entered into the column immediately after the flooding was complete.

2. DURATION OF EXPERIMENTS

Each experiment was continued until a state of apparently steady performance had been attained for a duration of at least one term. Thus it was assumed that the condition of the extraction column had represented a state of coordination or poise among the particular regime of operation, the resulting process, and the associated condition of the material under treatment, for a time at least as long as the term that the cossettes were retained in the process. The minimum acceptable duration for an experiment on this basis would seem to be about four terms. Most of them exceeded this, as indicated in the column headed "Number of column lengths worked" in table 7.

[4] J. Research NBS 15, 444 (1935) RP840; Ind. Eng. Chem. 27, 1268 (1935).
[5] J. Research NBS 15, 446 (1935) RP840; Ind. Eng. Chem. 27, 1268 (1935).

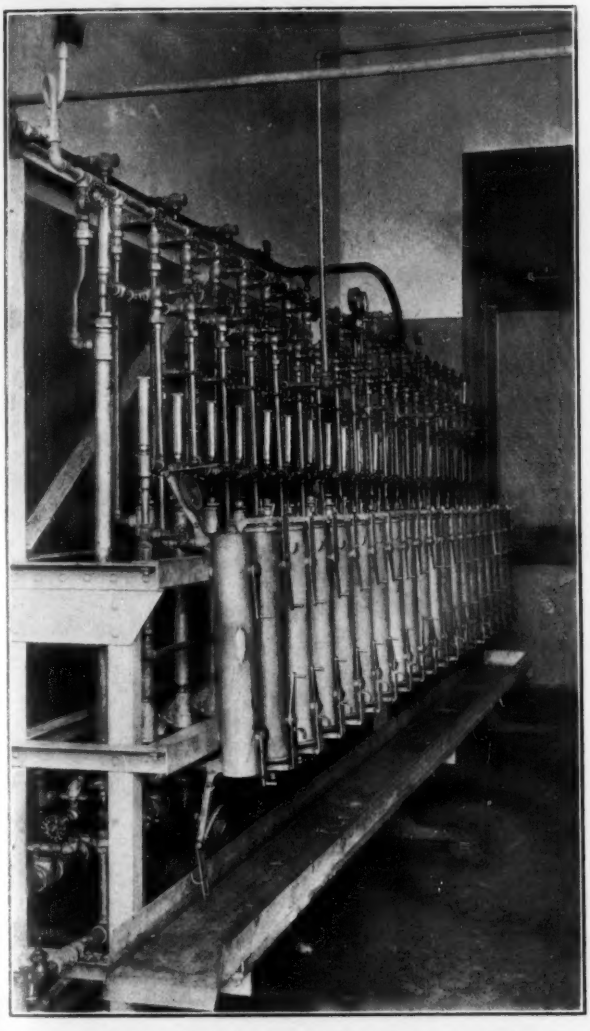

FIGURE 1.—*Miniature battery with cells arranged in straight row.*

The structure and equipment of the battery in both the straight and folded-row arrangements have been described in detail in a previous paper (RP840).

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3. ENDING THE RUN

The experiments were terminated in two ways: generally by "sweetening off", occasionally by "dropping" the whole material column at once for the purpose of "column sampling." The sweetening off was accomplished in a manner approximating commercial practice, except that in shortening the column, cells were dropped out of service only after they had served as the water inlet while the estimated average efflux weight of extract was being drawn into the draft receiver, rather than while the draft quantity only was being removed. When the concentration of reducing sugars in the extract had fallen to 1 percent or less, the operations were terminated and the remaining charges were discarded as residues. This condition was usually attained when the material column had been shortened by slightly less than half its regular operating length for that experiment. Table 1 compares the output performances attained in several experiments during regular operation and during the sweetening off.

TABLE 1.—*Comparison of output performance during sweetening off with that accomplished during regular operation in several experiments*

1925	Product	Reducing sugars expressed as—	Average for—	
			Regular regime	Sweetening off
July 9	Diffusion juice	Percentage	9.08	4.48
9	Pulp sap	g/100 ml	0.312	0.450
9	Pulp water	g/100 ml	.055	.238
13	Diffusion juice	Percentage	10.03	5.74
13	Pulp sap	g/100 ml	0.313	0.357
13	Pulp water	g/100 ml	.080	.187
16	Diffusion juice	Percentage	9.13	5.88
24	Pulp sap	g/100 ml	0.355	0.708
24	Pulp water	g/100 ml	.081	.212
30	Pulp sap	g/100 ml	.326	.594
30	Pulp water	g/100 ml	.095	.309
Average	Diffusion juice	Percentage	9.43	5.37
	Pulp sap	g/100 ml	0.327	0.545
	Pulp water	g/100 ml	.078	.239

4. SAMPLING OF MATERIAL COLUMN

In order to study the mode of the performance of an extraction process of this type it is necessary to know the residual concentrations existing in the sap of the particles and in the associated flood liquid at several levels [6] along the column at a particular instant whose relation to a period is known. The necessary observations require the withdrawal of samples of a size which would destroy the working characteristics of a column so small as any of those studied. For this reason column sampling has been accomplished only by suddenly discharging the whole contents of the battery without previous disturbance of the prevailing regular operation. Each sample comprises the whole contents of a cell, separated immediately into two parts, the chips and the flood liquid.[7] Since each part represents the respective mean for the whole cell, which is a considerable section of the column,

[6] J. Research NBS **15**, 446 (1935) RP840; Ind. Eng. Chem. **27**, 1268 (1935).
[7] J. Research NBS **15**, 458 (1935) RP840; Ind. Eng. Chem. **27**, 1273 (1935).

the concentrations are assumed to represent the existing conditions at the center of the cell. Thus to obtain results which can be interpreted with precision, it is necessary to sample several cells and preferable to sample them all. Moreover, the sampling must be completed within an interval of time which is short enough to be considered practically instantaneous.

(a) METHOD OF SAMPLING

When the operation of the column is about to be terminated, several experienced operators are stationed at even intervals along its length and a sample receiver is placed under each cell to be sampled. Precisely at the instant planned, the water input to the column is stopped and the whole contents of each cell are dumped into the tray of its respective receiver. The operations are performed as rapidly as possible and as nearly simultaneously as the several operators can act. Each receiver with its contents is weighed during the 5-minute interval allowed for draining. At the end of this interval the trays are removed, their contents transferred to individual closed containers, and each bucket with its contents of flood liquid is weighed. The pressed-out cossette sap and the flood liquid from each sample are analyzed separately.[8] For the present purpose the rapid method [9] is not recommended, although it may be used for samples taken near the head of the column.

(b) RESULTS OF COLUMN SAMPLING

The concentrations observed in three columns of material which were sampled and tested as specified above are presented in table 2. The listed concentrations are those observed in the prepared samples at 20° C; they require correction for the conditions of temperature as they existed in the material under operation. For the two July experiments included in this group, the temperatures observed at 15-minute intervals in the flood liquid issuing from each posture were recorded. The means of these observations for the respective whole runs are included in table 6. The temperatures observed during an interval of time coinciding approximately with the duration of retention of the "oldest" cossettes in the respective columns at the instant of sampling are presented in tables 3 and 4. The lines and arrows in each table indicate the progressive conditions of temperature for this "oldest" charge during the major portion of its life history and the last column of figures in each table indicates the mean of all the observations taken for each posture during the time that this charge was actually in process. Comparison of these two columns respectively with items 10 and 11 of table 6 reveals that the mean temperatures for this interval in each case were similar to the means for the run as a whole. The temperature control in the April experiment was not very different.

[8] BS J. Research **9**, 604 (1932) RP495.
[9] BS J. Research **9**, 607 (1932) RP495.

TABLE 2.—*Attenuation gradients of sampled columns*

Observed concentrations of reducing sugars in cossette input and diffusion juice output, in percent by weight; and in residue output and in cell contents of sap and flood liquid under processing, stated in g/100 ml at room temperature. The (apparent) head is the difference between the sap and flood liquid concentrations during processing.

	Item number (tables 9 to 14)		
	4	10	13
	Apr. 3, 1925	July 17, 1925	July 23, 1925
REDUCING SUGARS IN COSSETTES			
	Percent 12.35	*Percent* 14.15	*Percent* 14.265
REDUCING SUGARS IN DIFFUSION JUICE			
	6.41	9.19	9.95

REDUCING SUGARS IN CELL CONTENTS

In posture no.	At start			At end			At start		
	Sap	Flood	Head	Sap	Flood	Head	Sap	Flood	Head
	g/100 ml	*g/100 ml*	*g/100 ml*	*g/100 ml*	*g/100 ml*	*g/100 ml*	*g/100 ml*	*g/100 ml*	*g/100 ml*
Residue	[1] 0.665	[1] 0.143	[1] 0.522	[2] 0.597	[2] 0.314	[2] 0.283	[1] 0.365	[1] 0.104	[1] 0.261
19							.522	.180	.342
18	1.150	.578	.572						
17	1.322	.967	.355						
16	1.951	1.464	.487				1.167	.878	.289
15	2.565	2.141	.424						
14	3.340	2.892	.448						
13	4.079	3.625	.454	.597	.314	.283	2.478	2.250	.228
12	4.880	4.562	.318						
11	5.760	5.210	.550						
10	6.521	6.040	.481	2.08	1.57	.51			
9	7.542	7.240	.302				5.136	4.76	.376
8	8.60	8.22	.38	3.68	2.77	.91			
7	9.72	9.34	.38						
6	10.81	10.75	.06				8.60	7.72	.88
5	12.15	11.46	.69	6.91	5.53	1.38			
4	13.05	11.99	1.06						
3	13.17	11.25	1.92	11.45	9.25	2.20	12.91	12.14	.77
2	13.68	10.72	2.96						
1	12.46	10.35	2.11	12.68	9.21	3.47	13.84	9.81	4.03

[1] Since these columns were sampled at the start of a period, the concentrations in the *n*th cell do not represent the final pulp and pulp water. The concentrations which would have existed at the end of the period had the process continued, are assumed to be equal to the means for the previously sampled residues.

[2] Since this column was sampled at the end of a period, the concentrations observed in the *n*th cell at the time of dropping the column are assumed to represent the condition of the material (at 20° C).

TABLE 3.—*Record of the temperatures observed at 15-minute intervals during approximately the time of retention of the particular charge of cossettes which at the time of sampling was situated in posture 13 of the material column in the experiment of July 17, 1925*

Posture	Time of retention of chips	Temperatures observed at—					Mean 1:15 to 2:00, inclusive
		1:00 p.m.[a]	1:15 p.m.	1:30 p.m.	1:45 p.m.	2:00 p.m.	
	Percentage of whole period	°C	°C	°C	°C	°C	°C
13	92.6	92	80	80	77	80	79.0
12	88.5	93	83	84	80	80	81.7
11	80.8	90	83	85	85	86	84.8
10	73.1	82	80	80	86	87	84.8
9	65.4	83	77	81	86	90	83.5
8	57.7	79	76	84	86	87	83.3
7	50.0	80	79	90	86	87	85.5
6	42.3	88	82	84	87	87	85.0
5	34.6	90	82	83	83	85	83.2
4	26.9	88	82	85	76	81	81.0
3	19.2	84	80	80	75	75	77.5
2	11.5	80	72	80	75	65	73.0
1[b]	3.8	78	72	78	72	50	68.0
Means:							
13 to 4	92.6 to 26.9	86.5	80.4	83.6	83.2	85.0	82.1
13 to 3	92.6 to 19.2	86.3	80.4	83.3	82.5	84.1	82.5
13 to 1	92.6 to 3.8	85.2	79.1	82.6	81.1	80.0	80.7

[a] Temperatures of column 15 minutes before chips in posture 13 at time of sampling were introduced into column; not included in means listed in last column of table.

[b] Chips in posture 1 at time of sampling were introduced into column approximately 15 minutes after the last temperature observation at 2:00 p. m.

Line follows temperature program of chips located in posture 1 at 1:15 p. m., in posture 11 at 2:00 p. m., and in posture 13 at time of sampling. Since the temperatures were observed at the heater exits, the actual temperatures of the cossettes in the first postures were considerably less than the values recorded.

TABLE 4.—*Record of the temperatures observed at 15-minute intervals during approximately the time of retention of the particular charge of cossettes which at the time of sampling was situated in posture 19 of the material column in the experiment of July 23, 1925*

Posture	Time of retention of chips	Temperatures observed at—							Mean 11:30 to 12:45, inclusive
		11:15 a. m.[a]	11:30 a. m.	11:45 a. m.	12:00 noon	12:15 p. m.	12:30 p. m.	12:45 p. m.	
	Percentage of whole period	°C	°C	°C	°C	°C	°C	°C	
19	97.4	80	85	85	86	85	81	76	83.0
18	92.1	85	85	87	80	85	81	80	83.0
17	86.8	82	85	85	84	85	81	85	84.2
16	81.6	80	86	80	86	83	82	86	83.8
15	76.3	82	86	82	85	80	82	80	82.5
14	71.1	83	87	84	87	82	82	80	83.7
13	65.8	84	85	82	85	83	84	87	84.3
12	60.5	85	85	84	85	84	81	87	84.3
11	55.3	83	85	81	84	84	80	87	83.5
10	50.0	83	85	75	85	85	81	87	83.0
9	44.7	83	85	84	85	83	83	85	84.2
8	39.5	82	85	83	85	80	84	85	83.7
7	34.2	81	85	84	85	80	84	85	83.7
6	28.9	82	83	85	81	81	84	85	83.2
5	23.7	81	80	81	78	84	83	84	81.7
4	18.4	75	77	72	78	83	80	84	79.0
3	13.2	80	65	75	78	80	78	76	75.3
2	7.9	68	74	55	80	70	70		69.8
1[b]	2.6	70				70	60		65.0
Means:									
19 to 5	97.4 to 23.7	82.4	84.8	82.8	84.1	82.9	82.2	83.9	83.5
19 to 4	97.4 to 18.4	81.9	84.3	82.1	83.7	82.9	82.1	83.9	83.2
19 to 1	97.4 to 2.6	80.5	82.7	80.2	83.2	81.4	80.1	83.5	81.1

[a] Temperatures of column approximately 12 minutes before the chips in posture 19 at the time of sampling were introduced into the material column; not included in the means listed in the last column of the table.

[b] Chips in posture 1 at the time of sampling were introduced into the column and immediately dropped into the sample receiver approximately 10 minutes after the last observations of the temperatures were made.

The line follows approximately the temperature program of the charge which was located in posture 1 at 11:30, in posture 16 at 12:45, and in posture 19 at the time of sampling. Since the temperatures were observed at heater exits, the actual temperatures of cossettes in first postures were considerably less than those recorded.

5. TEMPERATURE MAINTENANCE AND RATES OF HEAT LOSSES

Although the heating of the newly charged cossettes through the operation of the flux is inadequate for a proper preparation of the material,[10] the capacity of the calorisators was found ample for this purpose as well as for the maintenance of suitable temperatures in the column, even at maximum steam pressures of 1-pound gage. To estimate the proportions of steam consumed in the primary heating and in the maintenance of temperatures under different conditions of room ventilation, three tests were made with water in place of cossettes and flood liquid. To appraise the rates of heat losses on the basis of exposed area as well as on the basis of the column length, the area of the exposed surfaces of the cells and manifolds without insulation was estimated by a detailed consideration of the various elements of the structure. The result is approximately 3.5 ft^2 per cell. In each of the three tests the column comprised 18 cells. Charges of 1 kg of cold water were introduced at 5-minute intervals, primed with the efflux from the column, and drawn at a rate similar to the drawing rates in the experimental extractions. From the total heat consumed

[10] J. Research NBS 15, 449 and 1269 (1935) RP840.

there was deducted the sum of the quantities recovered (1) in the water discharged as "residues" at the head of the column; (2) as "draft" at the foot; and (3) in the condensate issuing from all calorisators and heaters. The remainder is assumed to have been heat lost to the surroundings by "radiation", but including that transferred by conduction and convection. The results are presented in table 5.

TABLE 5.—*Estimated rates of heat loss from the experimental battery*

Test	Duration of test	Average temperature battery	Temperature of room	Temperature difference	Total heat in steam consumed	Heat consumed in heating water	Total heat lost to surroundings through "radiation"	Rate of loss in 18 cells		Rate of loss per cell	Over-all coefficient of heat transfer per square foot of surface
								Temperature difference	Temperature difference		
	min.	°C	°C	°C	kc	kc	kc	kc/hr/°C	Btu/hr/°F	Btu/hr/°F	Btu/hr/°F
1	24	72.7	26.0	46.7	6,351	1,721	4,630	247.6	546.0	30.33	8.67
2	19	73.0	26.0	47.0	5,070	1,711	3,359	225.7	497.7	27.65	7.88
3	24	54.0	28.0	26.0	5,238	1,438	3,755	361.0	796.2	44.23	12.64
Mean								278	613	34	9.7

The fact that the ventilation of the room was considerably better during the third test than during the others may account for the greater rate of heat loss in this case. Of the total heat consumed, the proportion lost was about the same in this test as in test 1, although the mean temperature of the battery was considerably less in test 3.

6. TEMPERATURE SCHEDULES

In most of the experiments the aim was to bring the cossettes to a temperature of about 80° C as rapidly as possible and to maintain this temperature during the remainder of the processing. In the experiment of July 23, the aim was to establish a temperature gradient from the head of the column to the middle. In two other experiments the aim was to maintain a steadily rising temperature during the retention of the cossettes. Table 6 presents the mean of all the observations of the temperature of the flood liquid taken at the heater exit of each posture in each July experiment; and tables 3 and 4 indicate the general run of variations among individual observations. Item 12a of table 6 presents the temperature schedule planned for the experiment of July 24; item 12b, the means of all the temperatures observed for each posture during the run. Since every value in each table represents the respective temperature after the flood liquid had received the increment supplied by the calorisator following the posture, it is more or less greater than the temperature which actually existed in the bottom of the posture. For the postures near the foot of any column the increments may have amounted to as much as 15°. It is for this reason that the installation of thermometers near the centers of the cells has been recommended in the construction of similar equipment.[11]

[11] J. Research NBS 15, 455 and 1272 (1935) RP840.

TABLE 6.—*Temperature schedules*

[Experiments for July 1925]

Each value listed is the observed (or planned) mean temperature for the posture indicated during the whole run of the experiment

Item	6	7	8	9	10	11	12a	12b	13
July	7	9	13	16	17	23	24	24	30
Schedule	Obs.	Obs.	Obs.	Obs.	Obs.	Obs.	Planned	Obs.	Obs.
Posture:	°C	°C	°C	°C	°C	°C	°C	°C	°C
19			81.4	83.3		81.9			
18	80.1		82.1	83.4		82.6	90.0	89.2	88.5
17	80.7	81.4	81.9	82.9		82.9	89.7	88.7	88.2
16	80.8	82.3	81.0	82.7		83.1	89.4	88.0	86.9
15	80.0	81.8	81.4	83.6		83.6	89.0	86.7	86.3
14	81.2	81.9	82.2	82.9		83.0	88.5	86.2	86.5
13	81.0	82.3	82.0	82.8	81.7	83.5	88.0	85.7	85.4
12	80.4	81.7	81.8	83.6	82.2	84.1	87.4	85.3	84.7
11	79.4	80.8	82.5	83.1	83.0	83.0	86.6	84.0	82.4
10	79.7	81.9	82.3	82.3	82.5	83.0	85.7	83.8	81.6
9	79.6	82.0	82.3	83.7	82.7	83.7	84.6	83.0	80.5
8	81.0	81.2	81.8	82.2	83.2	82.3	83.4	82.1	77.7
7	80.4	80.8	80.9	82.3	83.8	83.2	81.4	79 3	76.7
6	80.5	81.0	80.0	81.5	84.7	82.5	79.0	77.0	76.2
5	81.8	80.7	79.2	80.2	84.2	81.7	76.2	75.8	73.6
4	81.6	81.1	78.7	78.3	82.5	81.3	73.0	74.2	69.0
3	80.8	81.2	73.0	73.8	78.9	75.7	69.5	70.9	68.6
2	77.8	79.9	72.1	70.0	70.8	70.9	65.5	68.9	60.0
1	72.6	78.7	66.8	68.4	66.8	72.8	60.0	58.6	51.5
Mean	80.0	81.2	79.7	80.6	80.5	81.3	81.5	80.4	78.0

Mean of all except columns 10 and 12a 80.3

7. WORKING VOLUMES

The mean volumetric capacity of a cell is assumed to be approximately 1.9 dm^3. The mean value found by weighing more than 100 cellfuls of water at about 20° C, from six fillings of the battery, is 1.884 dm^3. The mean value calculated from the observed dimensions of the cells is the same. The index of variability of the weighings is equivalent to about 0.027 dm^3, and the maximum deviation from the mean is about 0.1 dm^3. Since the greater part of the indicated variation is due to differences in the capacities of the cells, rather than to accidental deviations in measurement, the cells are by no means uniform in size. Allowing for the expansion of cast brass between 20 and 80° C indicates a mean volumetric capacity of approximately the 1.9 dm^3 assumed as a round value. This probably allows for only a part of the flood liquid in the transfer ducts.

The working volume of the flood liquid per cell is assumed to have been equal to the difference between the mean volumetric capacity of a cell and the displacement volume of the mean charge of cossettes for each experiment, all at 80° C. The displacement volume of 1 kg of cossettes is assumed to have been the sum of the volumes occupied by 30 g of marc and 970 g of virgin sap. In all cases the 30 g of marc is supposed to have occupied a volume of 0.01736 dm^3 at the operating temperature of the battery. This is approximately the mean of several quantitative estimations obtained by extracting cossettes prepared from artichoke tubers from various sources, but it does not represent directly any of the material used in the extractions here reported. In each case the density of the virgin sap is calculated on

the assumption that it is due to the presence in the sap of all the reducing sugars observed in the cossettes, accompanied by such a quantity of other solid substances as to yield an apparent purity of 84.75 percent reducing sugars, and that all of these dissolved substances affect the density in the same way as levulose. Thus the density of the sap is equal to the density of a solution containing

$$S/(0.97\times 0.8475)=1.2165\ S$$

percent of levulose, where S stands for the observed percentage of reducing sugars in the cossettes, as indicated by the means of all the tests for each particular experiment. The volumes thus estimated are assumed to have remained constant throughout the processing of each charge of cossettes. To make sure that no considerable quantity of flood liquid became displaced through gas accumulation, frequent bleeder-cock tests were made on all cells during the course of each experiment. Since the amount of the draft was determined by drawing a constant weight of juice per period, as chosen at the start of each experiment (table 8), the resulting volume of draft per period is calculated on the basis of the average density at the average issuing temperature, which was usually in the neighborhood of 40° C.

This whole procedure greatly simplifies the calculations and yields results not essentially different from those which would have been obtained by a much more elaborate procedure based on individual weighings for each period, as was verified in a few experiments. No measurements of cossette dimensions were made on the material actually employed in the extraction experiments. Instead, the gross area of the diffusion layers in each case is assumed to have been 2.6 m^2/dm^3 of the calculated displacement volume of the cossettes, as estimated for a different lot of material and previously reported.[11] No corrections are essayed for the effects of either the adherent films or the area rendered ineffective through contacts of surfaces.

III. TYPICAL EXTRACTION DATA

The principal recorded data on the charging, operation, and over-all performance of the extraction columns established in 13 early experiments conducted in the straight arrangement of the cells are presented in tables 7 to 13, inclusive. These experiments include the three in which the column was sampled at the end of the run, with the results already presented in table 2. They include also the five experiments in which data on the performance during sweetening off are compared with those during normal operation (table 1).

Of the three sampled columns, two may be classed as long, the other as of medium length. In this sense length applies to the term of processing, rather than to the physical dimensions of the equipment; and it refers to the extraction of polysaccharides from artichoke cossettes of the dimensions specified, not to the diffusion of other material. In beet sugar practice a 13-cell column might be considered long rather than of medium length. The general set-up of each column is presented in table 7. A brief of the operating data (exclusive of temperatures, table 6) is presented in table 8.

[11] J. Research NBS 17, 615 (1936) RP931.

TABLE 7.—*Data on set-up of columns and durations of runs in 13 experiments*

A=total or average for April; *B*=total or average for July; *C*=total or average for July exclusive of July 17; *D*=total or average for all experiments in the list

Item	Date of run, 1925	Total weight of chips worked	Number of cells			Number of column lengths worked	Weight of chips in charge	Displacement volume of cossettes	Cell fill		Gross area of surface	Duration of	
			Charged	Drawn	In column				By volume	By weight		Mean period	Term of processing
		kg					kg/cell	dm³/cell	*Percent*	lb/ft³	m	min	min
1	Mar. 16	97.077	77		18	4.3	[a] 1.0000	[a] 0.9243					
2	Apr. 1	112.488	122	116	18	6.8	.9220	.8688	45.73	30.30	1.790	4.70	84.6
3	3	94.071	84	73	18	4.7	1.1200	1.0533	55.44	36.81	2.170	4.87	87.66
5	July 2	133.198	128	118	18	7.1	1.0406	.9736	51.24	34.20	2.006	4.95	89.1
6	7	91.293	74	65	18	4.1	1.2337	1.1539	60.73	40.55	2.377	6.00	108.0
7	9	99.595	101	91	17	5.9	.9861	.9243	48.65	32.41	1.904	5.00	85.0
8	13	98.567	93	83	19	4.9	1.0599	.9876	51.98	34.83	2.034	5.00	95.0
9	16	82.458	91	81	19	4.8	.9061	.8479	44.63	29.78	1.747	5.00	95.0
10	17	99.706	97	91	13	7.5	1.0279	.9582	50.43	33.78	1.974	4.90	63.7
11	23	83.140	75	65	19	3.9	1.1085	1.0328	54.36	36.43	2.128	4.80	91.2
12	24	76.576	73	64	18	4.1	1.0490	.9759	51.36	34.48	2.010	5.00	90.0
13	30	91.975	88	78	18	4.9	1.0452	.9753	51.33	34.35	2.009	5.00	90.0
Totals:													
A (3 runs)		303.636	283	(195)	54								
B (9 runs)		856.508	820	736	159								
C (8 runs)		756.802	723	645	146								
D (12 runs)		1,160.438	1,103	(931)	213								
Means:													
A (3 runs)		101.212	94		18	5.6	1.0729	1.0100	53.16	35.26	2.081	(4.79)	(86.22)
B (9 runs)		95.168	91	82	17.7	5.16	1.0445	.9753	51.33	34.33	2.009	5.07	89.74
C (8 runs)		94.600	90	81	18.25	4.95	1.0468	.9776	51.45	34.40	2.014	5.09	92.89
D (12 runs)		96.703	92	85	17.75	5.18	1.0518	.9846	51.82	34.57	2.028	(5.00)	(88.75)

[a] For this one run the displacement volume is expressed as dm³/kg, since the mean charge is not recorded.

TABLE 8.—*Brief of data on operation exclusive of temperatures*

A=total or average for April; *B*=total or average for July; *C*=total or average for July exclusive of July 17; *D*=total or average for all experiments in the list

Item	Date of run, 1925	Draft		Working volume				Volume of flood column [2]	Flood ratio [3]	Flux ratio [4]	Chip advancement [5]	Flood recession	
		By weight	On chips	Of draft	Of sap	Of flood	Of flux [1]					Per minute [6]	Relative [7]
		kg / *period*	*Percent*	dm³ / *period*	dm³ / *cell*	dm³ / *cell*	dm³ / *period*	dm³			*Percent* / *minute*	*Percent* / *minute*	*Percent* / *percent*
2	Apr. 1	1.493	118	1.4626	1.1646	0.7136	2.1762	12.844	0.613	1.869			2.05
3	2	1.493	162	1.4620	.8528	1.0312	2.4932	18.562	1.209	2.924	1.18	1.68	1.42
4	3	1.493	133	1.4641	1.0338	.8467	2.3108	15.241	.819	2.235	1.14	1.97	1.73
5	July 2	1.421	137	1.3781	.9555	.9264	2.3045	16.676	.970	2.412	1.12	1.67	1.49
6	7	1.420	115	1.3809	1.1325	.7461	2.1270	13.430	.659	1.878	.93	1.71	1.85
7	9	1.411	143	1.3672	.9072	.9757	2.3429	16.587	1.076	2.583	1.18	1.65	1.40
8	13	1.421	134	1.3706	.9692	.9124	2.2830	17.336	.941	2.356	1.05	1.58	1.50
9	16	1.440	150	1.3949	.8322	1.0521	2.4470	19.990	1.264	2.940	1.05	1.40	1.33
10	17	1.417	138	1.3714	.9404	.9418	2.3132	12.243	1.001	2.460	1.57	2.29	1.46
11	23	1.400	127	1.3501	1.0136	.8672	2.2173	16.477	.856	2.188	1.10	1.71	1.56
12	24	1.402	134	1.3544	.9577	.9241	2.2785	16.634	.965	2.379	1.11	1.63	1.47
13	30	1.430	137	1.3861	.9572	.9247	2.3108	16.645	.966	2.414	1.11	1.67	1.50
Totals:													
A (3 runs)		4.479											
B (9 runs)		12.762											
C (8 runs)		11.345											
D (12 runs)		17.241											
Means:													
A (3 runs)		1.493	139	1.4608	.9913	.8900	2.3508	16.020	.898	2.371	1.16	1.90	1.64
B (9 runs)		1.418	136	1.3727	.9571	.9247	2.2974	16.367	.966	2.400	1.11	1.65	1.48
C (8 runs)		1.418	135	1.3726	.9594	.9225	2.2951	16.836	.962	2.392	1.08	1.60	1.49
D (12 runs)		1.437	137	1.3948	.9663	.9154	2.3102	16.248	.947	2.391	1.13	1.72	1.52

[1] Volume of flux = volume of draft + volume of flood.
[2] Volume of flood column = n times volume of flood/cell.
[3] Flood ratio = $\frac{\text{volume of flood}}{\text{volume of sap}} = \frac{v''}{v'}$.
[4] Flux ratio = $\frac{\text{volume of flux}}{\text{volume of sap}} = \frac{f'}{v'}$.
[5] Rate of chip advancement, percentage of column-length/min.
[6] Rate as percentage of column-length/min.
[7] Rate expressed as column-length per period or percentage of column-length during 1 percent of the term.

1. GROSS RATES OF EXTRACTION

Data pertaining to the gross rates of extraction attained in the 13 experiments are presented in table 9. Comparing the over-all performance of the 13-cell column (item 10) with the mean for all of the longer columns set up in July (average *C*), it will be seen that the column of medium length produced a lower gross extraction (92.5 percent vs. 97.4 percent), of which a greater proportion (0.92 percent vs. 0.50 percent) was discarded in the pulp water. If the ultimate objective is continuous extraction in a true sense, this is an important consideration; for in the intermittent process the polysaccharides discarded in the pulp water were extracted, although not recovered. The mean rate of the gross extraction for the whole column was decidedly greater in the shorter column (1.01 g/m^2/min vs. 0.762 g/m^2/ min), although the relative flood recession per period was slightly less (1.46 vs. 1.49, table 8). Any error in the assumption that the effective areas of the diffusion layers were strictly proportional to the respective displacement volumes of the cossettes probably would influence the calculated rates not very differently in the two cases. The fact that relatively little change appeared in the analyses of the cossettes during July [13] leads to the belief that with the constant knife setting employed any variations in the dimensions of the cossettes influenced the rates of diffusion negligibly compared with the effects due to variations in the density of filling. Very probably when the density of filling passes a certain critical value which has not been determined definitely, the available area cannot remain directly proportional to the displacement volume but must fall off at an accelerating rate. The data *per se* present no obvious evidence that this value was exceeded in more than one experiment among the 8 included in average *C*. Not excluding this one experiment of July 7, the mean density of filling was but 0.6 lb/ft^3 greater in the longer columns. The mean temperatures for the respective whole runs were practically identical (80.5° vs. 80.3°).

[13] The cossettes were all cut from the same general lot of tubers kept under cold storage. The tubers for each experiment were removed on the day they were to be sliced.

TABLE 9.—*Gross extraction*

Item	Date of run, 1925	Analysis of cossettes		Reducing sugars at 80° C		Weight of reducing sugars per cell in—			Extracted in whole column		Mean rate of extraction for whole column	
		Levulose	Reducing sugars	In pulp sap [1]	In pulp water [1]	Fresh sap	Pulp sap	Pulp water	Period	On charge		
		Percent	*Percent*	g/100 ml	g/100 ml	g	g	g	g	*Percent*	g/m² *period*	g/m² *minute*
1	Mar. 16	8.7	12.2	1.100			[3] 11.00		[3] 120.99	91.67	3.47	
	16	8.65	12.3	1.227	0.256		[3] 12.27	[3] 2.56	[3] 119.72	90.70	3.43	
	16	8.25	11.9	2.317	.276		[3] 23.17	[3] 2.76	[3] 108.82	82.45	3.12	
	16	8.65	12.4	4.275			[3] 42.75		[3] 89.24	67.61	2.56	
	16			4.401			[3] 44.01		[3] 87.96	66.66	2.52	
Average		8.563	12.20	2.665	.266	[3] 131.99	[3] 26.63	[3] 2.66	[3] 105.36	79.82	3.02	(0.604)
2	Apr. 1	9.34	12.72	3.320	.356		38.66	2.54	116.75	75.12	2.65	
	1		12.54	2.201			25.63		128.78	82.86	2.93	
	1		11.72	.750	.178		8.73	1.27	146.68	94.38	3.33	
	1			.701	.083		8.16	.59	147.25	94.75	3.35	
Average		9.34	12.327	1.743	.205	155.41	20.30	1.46	135.11	86.94	3.07	(0.614)
3	Apr. 2	9.81	11.74	.944	.350		8.05	3.60	103.07	92.76	3.12	
	2	9.26	12.35	.964	.224		8.22	2.31	102.90	92.60	3.19	
	2			.252	.136		2.15	1.40	108.97	98.07	3.38	
	2			.633	.117		5.40	1.21	105.72	95.14	3.28	
	2			.789	.127		6.73	1.31	104.39	93.94	3.24	
Average		9.535	12.065	.796	.191	111.12	6.79	1.97	104.33	93.89	3.24	0.689
4	Apr. 3	9.06	12.35	.341	.068		3.53	.58	134.79	97.45	3.45	
	3			.624	.136		6.45	1.15	131.87	95.34	3.38	
	3			.633	.117		6.54	.99	131.78	95.27	3.37	
	3			.994	.234		10.28	1.98	128.04	92.57	3.28	
Average		9.06	12.35	.648	.139	138.32	6.70	1.18	131.62	95.16	3.37	.692
5	July 2	10.65	13.82	1.402	.104		13.40	.96	127.39	90.48	3.53	
	2	10.40	13.24	1.908	.093		18.23	.88	122.56	87.07	3.39	
	2			1.032	.135		9.86	1.25	130.93	93.00	3.63	
	2			.662	.153		6.33	1.42	134.46	95.50	3.72	
	2			.662	.181		6.33	1.68	134.46	95.50	3.72	
Average		10.525	13.53	1.133	.133	140.79	10.83	1.23	129.96	92.31	3.60	.727
9	July 7	10.32	13.58	.166	.027		1.88	.30	165.96	93.93	3.63	

6	July	7	10.32	13.58	.166	.027		1.88	.20	165.66	98.88	3.87	
		7			.182	.021		2.08	.16	165.48	98.77	3.87	
Average			10.32	13.58	.174	.024	167.54	1.97	.18	165.57	98.82	3.87	.645
7	July	9	9.46	12.67	.161	.040		1.46	.39	128.26	98.87	3.96	
		9	10.71	13.64	.363	.085		3.29	.83	126.43	97.46	3.91	
		9			.214	.050		1.94	.49	127.78	98.50	3.95	
		9			.477	.072		4.33	.70	125.39	96.66	3.87	
Average			10.085	13.155	.308	.054	129.72	2.79	.53	126.93	97.86	3.92	.784
Sweetening off; not in average					.438	.232		3.97	2.26	125.75	96.94	3.89	
8	July	13	11.13	14.51	.334	.062		3.74	.57	148.46	97.54	3 84	
		13	10.47	14.21	.354	.085		3.43	.78	148.77	97.75	3.85	
		13			.283	.087		2.74	.79	149.46	98.20	3.87	
		13			.248			2.40		149.80	98.42	3.88	
Average			10.80	14.36	.305	.078	152.20	2.96	.71	149.24	98.06	3.86	.772
Sweetening off; not in average					.348	.182		3.37	1.66	148.83	97.79	3.85	
9	July	16	10.06	13.49	.217			1.81		120.42	98.52	3.63	
		16			.270			2.25		119.98	98.16	3.61	
		16			.311	.064		2.59	.67	119.64	97.88	3.60	
Average			10.06	13.49	.266	.064	122.23	2.21	.67	120.02	98.19	3.62	.723
Sweetening off, not in average													
10	July	17	10.46	13.98	.561	.095		5.28	.89	140.17	96.37	5.46	
		17	10.59	14.32	.691	.138		6.50	1.30	138.95	95.53	5.41	
		17			.739	.135		6.95	1.27	138.50	95.22	5.40	
		17			.826	.178		7.77	1.68	137.68	94.66	5.37	
		17			.784	.151		7.37	1.42	138.08	94.93	5.38	
		17			.848	.132		7.97	1.24	137.48	94.52	5.36	
Average			10.525	14.15	.741	.138	145.45	6.97	1.27	138.48	95.21	5.40	1.101
11	July	23	10.73	14.50	.321	.090		3.25	.78	154.88	97.94	3.83	
		23	10.83	14.03	.489	.090		4.96	.78	153.17	96.86	3.79	
		23			.258	.126		2.61	1.09	155.52	98.35	3.85	
Average			10.78	14.265	.356	.101	158.13	3.61	.88	154.52	97.72	3.82	.796

[1] Assuming the expansion of the liquids in the April 3, the July 17, and the 23 experiments was 0.44 ml/dm³/° between 20 and 80° C; and for all other experiments, 0.45 ml/dm³/°.
[2] Including the amount discarded in the pulp water, since this also diffused during the period.
[3] For this 1 experiment, per liter of liquid, not per cell.

TABLE 9.—*Gross extraction*—Continued

Item	Date of run, 1925	Analysis of cossettes		Reducing sugars at 80° C		Weight of reducing sugars per cell in—			Extracted in whole column		Mean rate of extraction for whole column	
		Levulose	Reducing sugars	In pulp sap	In pulp water	Fresh sap	Pulp sap	Pulp water	Period	On charge		
		Percent	*Percent*	g/100 ml	g/100 ml	g	g	g	g	*Percent*	g/m *period*	g/m *minute*
12	July 24	10.75	14.69	.423	.068		4.05	.63	150.00	97.37	4.15	
	24	10.89	14.68	.326	.084		3.12	.78	150.93	97.97	4.17	
	24			.288	.086		2.76	.79	151.29	98.21	4.18	
Average		10.82	14.685	.346	.079	154.05	3.31	.73	150.74	97.85	4.17	.833
Sweetening off, not in average				.689	.206		6.60	1.90	147.45	95.72	4.08	
13	July 30	10.74	14.18	.239	.073		2.29	.68	144.77	98.44	4.00	
	30	10.78	13.96	.407	.111		3.90	1.03	143.16	97.35	3.96	
	30			.307	.093		2.94	.86	144.12	98.00	3.99	
Average		10.76	14.07	.317	.093	147.06	3.03	.86	144.03	97.94	3.98	.797
Sweetening off, not in average				.569	.301		5.45	2.78	141.61	96.29	3.92	
Totals:												
A		[1] 307.13				404.85	33.79	4.61	371.06			
B		[1] 995.56				1,317.17	37.68	7.06	1,279.49			
C		[1] 887.37				1,171.72	30.71	5.79	1,141.01			
D		[1] 1,302.69				1,722.02	71.47	11.67	1,650.55			
Averages:												
A		9.542	12.578	1.136	.173	134.95	11.26	1.54	123.69	91.65	3.30	(.689)
B		10.591	14.012	.437	.085	146.35	4.18	.78	142.17	97.14	4.00	.789
C		10.396	13.992	.400	.078	146.47	3.84	.72	142.63	97.38	3.88	.762
D		10.321	13.643	.616	.106	143.50	5.95	.97	137.55	95.86	3.82	.764

[1] Grams of levulose per cell. The average quantity of levulose per 100 reducing sugar is 75.65; of reducing sugar per 100 levulose, 132.19.

Apparently the difference in the mean gross rates of extraction was due to differences in the operating conditions produced by variation in the length of the terms of processing and in the velocities of phase translation. Thus the mean rate of extraction per minute for the eight longer columns was 69.2 percent of the mean rate attained in the column of medium length; while the mean flux velocity per minute was 69.4 percent, and the reciprocal duration of term 68.6 percent of the respective values for the column of medium length.

That the saccharides containing the greater proportions of levulose were not preferentially retarded during diffusion is indicated by the fact that the levulose ratio (stated in table 10 as parts of levulose in 100 parts of reducing sugars) was not less in the diffusion juice than in the cossettes, and not greater in the residues (of pulp and pulp water) than in the cossetes. The mean of all tests made in connection with these experiments indicates that the polysaccharides of the cossettes yielded upon hydrolysis about three-fourths levulose and one-fourth other reducing sugars. Some interesting relations among the relative proportions of levulose, other reducing sugars, and soluble substances not classified as sugars are presented in table 11.

TABLE 10.—*Yield of residues and analytical data on diffusion juice*

Item	Date of run, 1925	Weight of residues per 100 g of cossettes		Analysis of diffusion juice					Levulose to reducing sugars				
				Density	Levulose	Reducing sugar	Dry substance	Ash	Diffusion juice	Cossettes	Residues		Converter liquor
		Wet pulp	Pulp water								Pulp	Pulp water	
		g	g	[a] *Brix*	*Percent*	*Percent*	*Percent*	*Parts/100 Brix*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
1	Mar. 16	-------	-------	-------	5.46	8.34	9.65	0.80	[b]65.5	70.2	68.1	67.4	71.1
2	Apr. 1	-------	-------	9.99	4.95	6.76	7.88	----------	73.2	73.4	-------	-------	-------
3	2	-------	-------	11.32	6.03	7.77	9.49	----------	77.6	79.0	-------	-------	-------
4	3	-------	-------	11.08	5.30	6.41	-------	----------	82.7	73.4	-------	-------	-------
5	July 2	97.6	99.2	11.89	6.86	8.88	10.73	.728	77.3	77.8	-------	-------	-------
6	7	101.3	111.6	10.96	6.66	8.31	10.19	.601	80.1	76.0	-------	-------	-------
7	9	94.7	85.3	10.16	7.02	9.08	-------	.555	77.3	76.7	-------	-------	-------
8	13	-------	-------	12.44	7.97	10.03	-------	----------	79.5	75.2	-------	-------	-------
9	July 16	93.6	84.7	10.66	7.10	9.13	-------	----------	77.8	74.6	-------	-------	-------
10	17	103.4	84.4	11.33	6.98	9.19	-------	----------	75.9	74.4	-------	-------	-------
11	23	104.4	71.4	12.25	7.58	9.95	11.60	.596	76.2	75.6	-------	-------	-------
12	24	104.1	78.0	11.89	7.38	9.71	10.96	.588	76.0	73.7	-------	-------	-------
13	30	105.1	80.0	11.34	7.04	9.00	10.57	----------	78.2	76.5	-------	-------	-------
Average		100.5	85.4	11.28	6.64	8.66	10.13	.645	76.70	75.65	68.1	67.4	71.1

[a] Not corrected to indicate dry substance equivalent to levulose; and not taken on the same sample used in the estimation of dry substance.

[b] This result seems erroneous, since the same juice converted yielded 71.1.

TABLE 11.—*Miscellaneous ratios among levulose, reducing sugars, and dry substance in diffusion juice*

Item	Date of experiment, 1925	Purity quotient based on—		Parts of total solids containing 100 parts of—		Reducing sugar "excess", on levulose
		Levulose	Reducing sugars	Levulose	Reducing sugars	
1	March 16	56.6	86.4	177	116	32.8
2	April 1	62.8	85.8	159	117	26.6
3	2	63.5	81.9	157	122	28.9
Mean of 3		61.0	84.7	164	118	30.4
5	July 2	63.9	82.8	156	121	29.5
6	7	65.4	81.6	153	123	24.8
11	23	65.3	85.8	153	117	31.3
12	24	67.3	88.6	149	113	31.6
13	30	66.6	85.1	150	117	27.8
Mean of 5		65.7	84.8	152	118	29.0
Mean of 8		63.9	* 84.75	156	* 118	32.9

* Values assumed in calculating densities, tables 7, 8, and 9.

2. RESIDUES

In all but one of the July experiments the pulp and pulp water were weighed as discharged. The mean relative weight of each, per hundredweight of cossettes, is presented in columns 3 and 4 of table 10. In the last three experiments samples of the wet pulp, after draining for 5 minutes, were pressed in a hand-operated screw tincture press and the pressed pulp was dried in a vacuum dryer provided with steam-heated shelves. Table 12 is a summary of the data obtained. The yield of dried pulp expressed as a percentage by weight of either the wet pulp or the original cossettes is somewhat less than the corresponding value for dried beet pulp.

TABLE 12.—*Data on pulp drying*

Date of experiment, 1925	Product	Percentage on—					
		Cossettes	Wet pulp	Pressed pulp	Cossettes	Wet pulp	Pressed pulp
		Experiment 1			Experiment 2		
July 23	Wet pulp	106.3	100.0	178.4	106.3	100.0	172.1
	Press water	45.3	42.6	78.4	44.5	41.9	72.1
	Pressed pulp	61.0	57.4	100.0	61.8	58.1	100.0
	Moisture dried out	56.3	53.0	92.2	57.4	54.0	93.0
	Dried pulp	4.7	4.4	7.8	4.4	4.1	7.0
		Experiment 3			Experiment 4		
July 24	Wet pulp	104.6	100.0	190.7	104.6	100.0	161.5
	Press water	49.8	47.6	90.7	39.8	38.1	61.5
	Pressed pulp	54.8	52.4	100.0	64.8	61.9	100.0
	Moisture dried out	50.5	48.3	92.2	59.7	57.0	92.0
	Dried pulp	4.3	4.1	7.8	5.1	4.9	8.0
		Experiment 5					
July 30	Wet pulp	100.3	100.0	224.5			
	Press water	55.6	55.5	124.5			
	Pressed pulp	44.5	44.5	100.0			
	Moisture dried out	40.4	40.4	90.7			
	Dried pulp	4.1	4.1	9.3			
		Averages of five experiments					
	Wet pulp		100.0				
	Press water		45.1				
	Pressed pulp		54.9				
	Moisture dried out		50.5				
	Dried pulp	4.5	4.3	8.0			

IV. SPECIAL REGIMES

1. EXTRACTION WITH PREHEATING

Other conditions being equivalent, the practice of preheating the cossettes before introducing them to the flux resulted in a higher concentration of the polysaccharides in the diffusion juice and in a smaller amount of rejectment of extractives in the residues. This was true whether the juice, which was circulated for heating, was acidified or not.

2. MIDCOLUMN DOSAGE WITH SULPHUR DIOXIDE

In devising the regime of midcolumn dosage[14] it was anticipated that certain classes of reagents might be eliminated from the residues at least as extensively as the original extractives. The results of a single experiment will serve to illustrate this effect.

(a) EXPERIMENTAL CONDITIONS

(1) *Experiment of May 7, 1928.*—Folded arrangement of cells in battery, with 18 cells under flux and no preheating. Charges uniform at 1.000 kg. Saturation of flood liquid with SO_2 applied during transit between postures 9 and 10 in a total volume of approximately 6.6 liters under circulation. Mean duration of retention in circulatory system, 13.3 minutes. Mean period, 4.72 minutes; mean term of retention of cossettes, 84.96 minutes. Mean temperature of material in diffusion zone and saturator, 70° C. Mean advancement of chips, 1.18 percent of column length per minute; mean flood recession, 1.50 cell lengths/period=1.76 percent of column length per minute. Mean operating level of liquid in saturator, 40 cm. Other details of the operating conditions are presented in tables 13 to 15, inclusive.

TABLE 13.—*Volumetric capacity of circulatory system*[1]

	Liters
Low-pressure manifold, ¾-inch pipe and fittings	1.434
Low-pressure manifold, ⅜-inch side connections and fittings	.502
Total	1.936
Circulation pump only	.330
High-pressure manifold, all ⅜-inch pipe and fittings	.787
Total, except saturator tank	3.053

VOLUMETRIC CAPACITY OF SATURATOR TANK AT VARIOUS OPERATING LEVELS

Gage	Capacity	Gage	Capacity	Gage	Capacity
cm	*Liters*	cm	*Liters*	cm	*Liters*
10.3	1.70	32.9	3.24	66.7	4.62
16.6	2.05	35.4	3.37	72.5	4.87
19.8	2.31	39.0	3.51	76.0	5.08
22.2	2.51	44.9	3.86	80.1	5.20
25.0	2.74	52.1	4.10	84.7	5.35
29.5	3.10	59.7	4.35	87.7	5.50

[1] The working capacity of the whole circulatory system could vary between the limits of 5 and 8 liters, and at the mean level employed in the experiment of May 7, 1928, its capacity was approximately 6.6 liters.

[14] J. Research NBS 15, 452 and 1271 (1935) RP840.

TABLE 14.—*Summary of operating volumes*

Item	Sap		Flood		Draft		Flux	
	Liters	Percentage on sap	Liters	Percentage on sap	Liters	Percentage on sap	Liters	Percentage on sap
Per cell or per period	0.944	100.0	0.939	99.5	1.407	149.0	2.346	248.5
In column:								
Below circulation	8.496	50.0	8.451	49.7				
Above circulation	8.496	50.0	8.451	49.7				
Total in cells	16.992	100.0	16.902	99.5				
In circulatory system			6.6	38.8				
In total flood column			23.5	138.3	1.407	8.28	2.346	13.81
Volume (per minute)	0.200	*0.85			0.298	*1.27	0.497	*2.11

* These percentages are computed on the total flood column, not the sap.

The desired pressure of the gaseous contents of the saturator was maintained by immersing the liquid-SO_2 cylinder in a steam-heated water-bath which was adjusted by hand to a temperature of approximately 30° C throughout the experiment. The pressure of the battery supply water was that produced by a small booster pump of the centrifugal type in series with the city water supply, and it averaged 54 lb/in.^{2} above atmospheric pressure. At the rate of flux employed an average head of 33 lb/in.^{2} was required to force the flood liquid through the upper half of the column, and the difference, 21 lb/in.^{2}, was the maximum mean pressure allowable for the gases in the scrubber, where the mean surface of the liquid was approximately level with the low pressure manifold. If the pressure due to air in the scrubber had been negligible, the temperature of the liquid SO_2 could not have exceeded 4 to 24°, although the temperature of the water-bath never was less than 26° C. Actually the pressure must have contained a considerable component due to air, since even the minimum pressure observed, if due to water vapor and SO_2 alone, should have established a greater concentration of the reagent in the diffusion juice than any observed. In coming to this conclusion, full account is taken of the dilution with respect to SO_2 due to diffusive interchange between sap and flood liquid in the lower half of the column. Unfortunately, no direct observations were made on the concentrations of SO_2 which existed in either the liquid or the gaseous contents of the saturator. Details of the pressures observed are presented in table 15. The gaseous pressure in the scrubber was approximately equal to the hydrostatic pressure in the low-pressure manifold at the mean operating level of 40 cm, which was maintained in the scrubber.

TABLE 15.—*Summary of pressures*

Time	Gage pressures					Temperature of water-bath	Absolute pressure of air, water vapor, and SO_2
	Battery supply water	Pressure drop to mid-column	In circulatory system				
			Low-pressure manifold	Developed by circulation pump	High-pressure manifold		
	lb/in.²	lb/in.²	lb/in.²	lb/in.²	lb/in.²	°C	atm
11:24 a. m.	52	14	38	8	46	30	3.59
11:45 a. m.	52	30	22	8	30	30	2.50
12:00 noon	54	36	18	8	26	26	2.22
12:05 p. m.	52	28	24	6	30	30	2.63
12:14 p. m.	----	----	36	8	44	----	3.45
12:30 p. m.	54	33	21	8	29	30	2.43
2:00 p. m.	48	31	17	8	25	30	2.16
3:14 p. m.	59	47	12	10	22	29	1.82
4:40 p. m.	60	47	13	8	21	----	1.88
Mean	54	33	21	8	27	29	2.37

(b) EXPERIMENTAL RESULTS

The concentrations of reducing sugars and SO_2 were observed in the resulting products for several of the periods. The results, as identified with the charges numbered serially from the beginning, are presented in table 16. The residues are those which resulted from the extraction of a given charge and the diffusion juice that which was drawn from the cell containing the given charge.

TABLE 16.—*Observed concentrations of* SO_2 *and reducing sugars in products*

Charge	Pulp sap		Pulp water		Diffusion juice	
	SO_2	Reducing sugar	SO_2	Reducing sugar	SO_2	Reducing sugar
	mg/100 ml	mg/100 ml	mg/100 ml	mg/100 ml	mg/100 ml	mg/100 ml
10	----	----	----	----	432.0	4,600
12	1.16	----	0.864	14.35	216.2	4,210
13	2.09	80.40	1.660	37.60	----	----
14	2.34	87.60	0.896	20.45	----	----
15	2.13	146.00	1.230	62.37	----	----
21	2.56	143.22	1.540	29.92	----	----
23	4.87	127.49	3.170	34.50	----	----
41	----	----	----	----	470.9	4,380
43	----	----	----	----	444.2	4,040
46	28.60	320.10	10.150	34.65	296.2	4,710
Total, charges 10 to 43	15.15	584.72	9.610	199.19	1,563.3	17,230
Average, charges 10 to 43	2.525	116.944	1.602	33.198	390.83	4,307.5

(c) RELATIVE EXTRACTIONS OF SULPHUR DIOXIDE

The performance of the process with respect to the removal of SO_2 from the residues relative to the concurrent extraction of reducing sugars is expressed very strikingly in table 17, which is calculated from table 16.

TABLE 17.—*Relative concentrations of extractives*

Extractives	Material in which contained	Concentration					
		Grams per 100 g of SO_2 in—			Grams per 100 g of reducing sugars in—		
		Pulp sap	Pulp water	Diffusion juice	Pulp sap	Pulp water	Diffusion juice
SO_2	Pulp sap	100.00	157.6	0.65	2.16	7.61	0.059
Reducing sugars	do	4,631	7,300	29.9	100.00	352.3	2.72
SO_2	Pulp water	63.44	100.00	.41	1.37	4.83	.037
Reducing sugars	do	1,315	2,072	8.49	28.4	100.00	.771
SO_2	Diffusion juice	15,480	24,400	100.00	334	1,177	9.07
Reducing sugars	do	170,600	268,900	1,102	3,683	12,980	100.00

Thus for every 100 g of SO_2 in the diffusion juice, the pulp sap contained but 0.65 g and the pulp water but 0.41 g; while for every 100 g of reducing sugars in the diffusion juice the pulp sap contained 2.71 g and the pulp water 0.77 g. The fact that the pulp sap contained relatively less than one-fourth as much SO_2 as reducing sugars and the pulp water relatively more than one-half as much SO_2 as reducing sugars was due to the fact that the reagent was diffusing more rapidly than the polysaccharides. The velocity of diffusion for the reagent was so much greater that the flood liquid (pulp water) in the last posture could attain a concentration of SO_2, which was 63 percent of that left in the sap while it was attaining a concentration of reducing sugars which was but 28 percent of that left in the sap (41/0.65=63; 77/2.71=28). The concentration of reagent could be reduced to 2.16 percent of the concentration of reducing sugars in the pulp sap by contact with flood liquid which thereby absorbed the reagent up to 4.83 percent of its concentration of reducing sugars. (Notice that all concentrations are expressed on a gram basis, not molecular. The molecular concentration of the polysaccharides cannot be stated, since the mean molecular weight is not known.)

TABLE 18.—*Brief of relative concentrations of extractives*

Extractives	Material in which contained	Percentage on SO_2 in diffusion juice	Percentage on reducing sugars in diffusion juice	g/100 g reducing sugars in material in which contained
SO_2	Pulp sap	0.65	0.059	2.16
	Pulp water	.41	.037	4.83
	Diffusion juice	100.00	9.073	9.07
Reducing sugars	Pulp sap	29.92	2.71	100.00
	Pulp water	8.40	.77	100.00
	Diffusion juice	1,102	100.00	100.00

The differentials in the relative extraction of the two kinds of extractives would have been still greater except that charges 21, 23, 41, 43, and especially 46, were discharged before the process was complete. The mechanical failure of the mass-structure of the packed cossettes had developed an excessive pressure-gradient in the upper half of the column, rendering it necessary to discard these particular charges be-

fore they had reached the head of the column. Table 15, column 3, indicates that this pressure-gradient had an upward trend throughout the experiment. For this reason and others it is concluded that the term of processing should have been shorter with this regime and this lot of tubers.

V. SUMMARY

The experimental procedure has been described for the ordinary regime of operation in the miniature diffusion battery previously described, including the method used in setting up the extraction columns and two methods used in terminating experiments. The gross performance of several columns during sweetening off has been compared with the previous performance during regular operation. The concentration gradients observed along the columns in three early experiments have been presented for future analysis. Data have been presented on the relative volumes of sap and flood liquid, the rates of phase translation, the temperatures of the flood liquid, the degree of extraction attained, and the relative magnitudes of the residues obtained in the extraction of polysaccharides from jerusalem artichoke cossettes prepared with commercial beet knives. This includes the yield of dried pulp in three experiments. The over-all rates of the gross extraction have been correlated with the rates of phase translation employed. Finally, the relative degree of extraction of the polysaccharides and an added reagent (SO_2) has been illustrated by means of the data obtained in a single experiment with the regime of midcolumn dosage previously described by one of us.

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OPTICAL SPECIFICATION OF LIGHT-SCATTERING MATERIALS

By Deane B. Judd

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ABSTRACT

In 1931 Kubelka and Munk worked out the relationship between reflectance and thickness of material for thin, homogeneous layers illuminated diffusely. In the equation expressing this relationship, the hypothetical ideal material is defined by two constants, reflectivity and coefficient of scatter. In the present paper are given data demonstrating how well several materials of commerce can be specified by these constants. These include data on vitreous enamel, dental silicate cement, cold-water paint, and paper.

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I. INTRODUCTION

Relations between the incident, reflected, and emergent light from a thin, homogeneous layer of absorbing and scattering material have been worked out in various forms.[1] Usually these relations have been developed in theory by considering perfectly diffused light incident on any elementary layer of the material which is assumed to absorb a portion, reflect diffusely another portion, and transmit diffusely the remainder. Traveling of the diffused light through the thin sheet of material has been considered, but scattering of light to the sides, or light lost through the edges of the material, has usually been left out of account because of the added complexity. Of the various derivations the most readily applicable to practical measurement is that of Kubelka and Munk, who carried through the derivation in such a way that the related quantities are those which are customarily measured. The equations of this important derivation have been reproduced and the discussion of them given in English by Steele.[2]

Measurements on materials result in values of reflectance which are related to thickness in a way somewhat different from that described by the Kubelka-Munk formula; first, because real materials differ from the ideal material assumed in the derivation by being inhomogeneous; second, because the reflectometers fail either to diffuse perfectly the light falling on the sample or to measure all light diffusely reflected, or both; third, because some light is lost through the edges of the samples; and, fourth, because the amounts of light absorbed and scattered by the materials vary according to the wave length of the light. The purpose of the present paper is to discover how large are the departures from theory due to these sources and to inquire whether a description of materials in terms of the simple Kubelka-Munk formulation is sufficiently exact to be of value.

II. DEFINITION OF TERMS

$R \equiv$ light reflectance of a specimen, or the fraction of incident light reflected from a specimen. (Except for the ideal, perfectly diffusing specimen, reflectance depends on the angular distribution of incident light.)

$A \equiv$ apparent light reflectance of a specimen, or the reflectance which an ideal, perfectly diffusing specimen would require in order to have the same brightness as the actual specimen under the same illuminating and viewing conditions. (In this work the illuminating and viewing conditions are chosen so as to avoid taking into account light specularly reflected from glossy specimens; the apparent light reflectance so taken has sometimes been called the diffuse reflectance.)

$R_\infty \equiv$ light reflectivity of the material, or the reflectance of an infinitely thick specimen of the material; that is, practically,

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[1] G. G. Stokes, *On the intensity of light reflected from or transmitted through a pile of plates*, Proc. Roy. Soc. (London) **11**, 545 (1860–62).
H. J. Channon, F. F. Renwick, and B. V. Storr, *The behavior of scattering media in fully diffused light*, Proc. Roy. Soc. (London) [A] **94**, 222 (1918).
L. Silberstein, *The transparency of turbid media*, Phil. Mag. [7], **4**, 1201 (1927).
M. Gurevich, *Ueber eine rationelle Klassification der lichtstreuenden Medien*, Physik. Z. **31**, 753 (1930).
J. W. Ryde and B. S. Cooper, *The scattering of light by turbid media*, Proc. Roy. Soc. (London) [A], **131**, 451 (1931).
P. Kubelka and F. Munk, *Ein Beitrag zur Optik der Farbanstriche*, Z. tech. Phys. **12**, 593 (1931).
T. Smith, *The hiding power of diffusing media*, Trans. Opt. Soc. **33**, 150 (1931–32).

[2] F. A. Steele, *The optical characteristics of paper. I. The mathematical relationships between basis weight, reflectance, contrast ratio and other optical properties*, Paper Trade J. **100**, no. 12, 37 (Mar. 21, 1935).

one so thick that a further increase in thickness does not change its reflectance.

$A_\infty \equiv$ apparent light reflectivity of the material.

$R_0 \equiv$ light reflectance of a specimen in contact with a backing of zero reflectance.

$R_1 \equiv$ light reflectance of a specimen in contact with a backing of unit (100 percent) reflectance.

$R_{R'} \equiv$ light reflectance of a specimen in contact with a backing of reflectance, R' $(0 \leq R' \leq 1)$.

A_0, A_1, and $A_{R'}$ refer to apparent light reflectances and are analogous to R_0, R_1, and $R_{R'}$, respectively.

$C \equiv R_0/R_1 \doteq A_0/A_1$, called ideal contrast ratio.

$C_{0.89} \equiv A_0/A_{0.89}$, called TAPPI opacity[3] provided the illumination be in effect perfectly diffused and the direction of view not more than 20° from normal.

$C_{R'} \equiv R_0/R_{R'} \doteq A_0/A_{R'}$, called simply contrast ratio.

$C_\infty \equiv A_0/A_\infty \doteq R_0/R_\infty$, called printing opacity if the material is paper.

$P \equiv C_{0.80}$ for an enamel coating of 6.0 g/dm², called covering power of a vitreous enamel.

$X \equiv$ thickness of the specimen (sometimes measured by weight per unit area, as in vitreous enamels, paint films, and paper; sometimes by volume per unit area, as in paste for cold-water paint.)

$S \equiv (dR_0/dX)_{X \to 0}$, called coefficient of scatter, the rate of increase of reflectance of a specimen with thickness for nearly zero thickness of specimen over a black backing.

$SX \equiv$ scattering power of a particular specimen consisting of a thickness, X, of material having coefficient of scatter, S.

III. APPARATUS AND METHOD

1. GENERAL METHOD

Attention has been confined in this paper chiefly to materials whose reflectance is fairly high and nearly nonselective with respect to wave length. These materials (whites and near-whites) may be expected to have reflectivities and coefficients of scatter nearly independent of the wave length of incident light and there is hope that single average values of reflectivity and coefficient of scatter may be found to represent them properly even when illuminated by light (such as daylight) of a considerable wave-length range. It is not to be expected that materials having highly chromatic colors can be so represented; such materials will require for their specification values of reflectivity and coefficient of scatter as functions of wave length.

Data on four classes of materials are reported in this paper. The general plan of the investigation for each class of materials is:

1. Select a number (3 to 5) of representative materials ranging in reflectivity from the highest to the lowest usual values.

2. Prepare from each material a number of specimens ranging in thickness from the thinnest usually encountered in practice up nearly to that of an opaque layer.

3. Measure apparent light reflectance for black backing, A_0, and for white backing, $A_{R'}$, where R', the reflectance of the backing, is between 0.70 and 0.90.

[3] Official method, T425 m-36, for testing opacity of paper; Technical Association of the Pulp and Paper Industry.

4. Check these experimental values, (A_0, $A_{R'}$) against the Kubelka-Munk formula on the assumption that A_0 and $A_{R'}$ are adequate approximations to R_0 and $R_{R'}$, respectively.

2. GRAPHICAL AIDS

A number of graphical aids for this comparison have been prepared and will now be described.

The Kubelka-Munk formula is

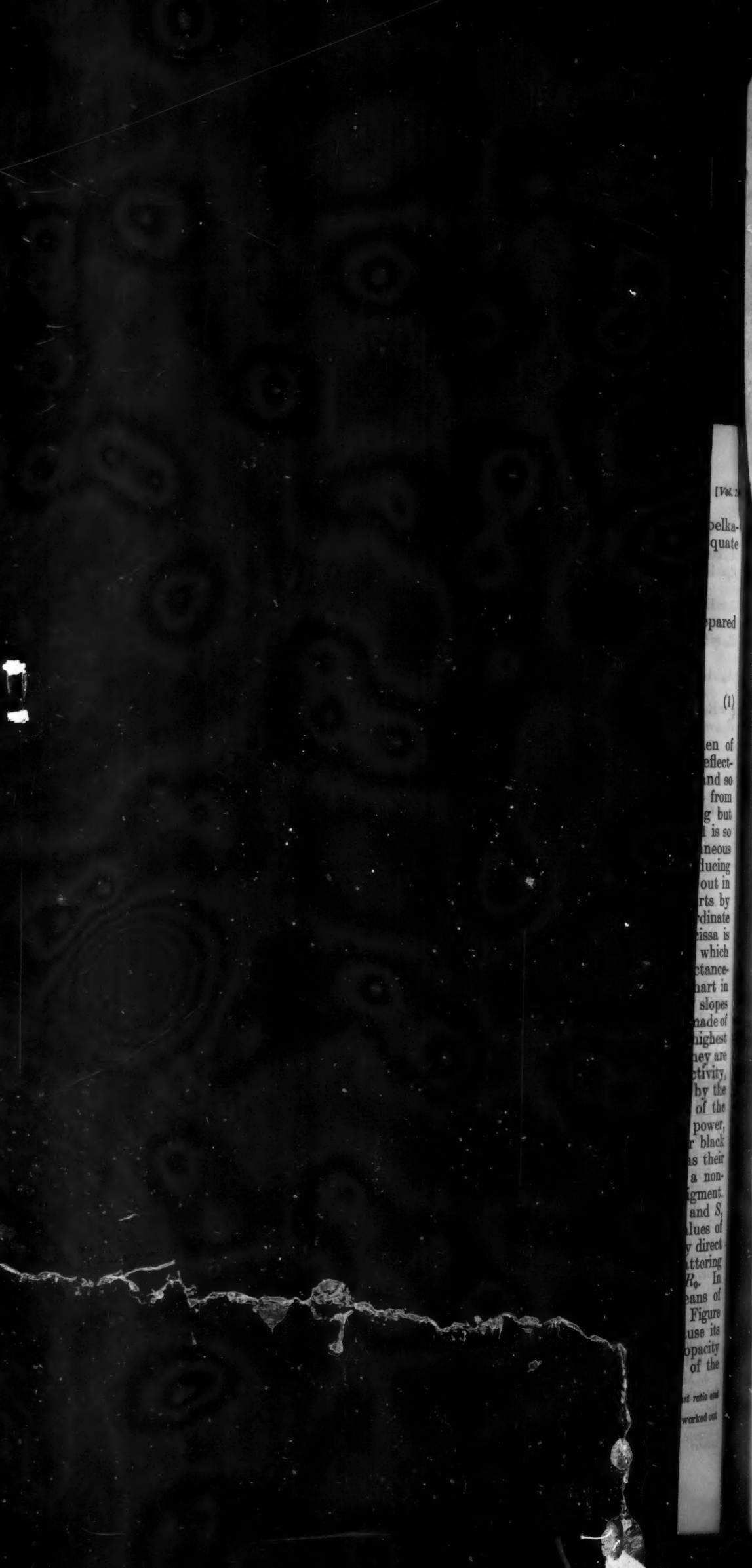
$$R_{R'}=\frac{(R'-R_\infty)/R_\infty-R_\infty(R'-1/R_\infty)e^{SX(1/R_\infty-R_\infty)}}{(R'-R_\infty)-(R'-1/R_\infty)e^{SX(1/R_\infty-R_\infty)}} \quad (1)$$

From two measurements of reflectance, $R_{R'}$, of a specimen of known thickness, X, one for each of two backings of different reflectance, R', it is possible to solve for R_∞ and S from equation 1 and so obtain a specification of the material. This can also be done from two measurements of reflectance made with the same backing but with samples of different thickness, X. The form of equation 1 is so little adapted, however, to easy solution of pairs of simultaneous equations of this sort that all of the solutions required for reducing the experimental data of the present study have been worked out in advance and expressed graphically on reflectance-opacity charts by families of curves for different values of SX and R_∞. The ordinate of these charts is reflectance, R_0, for black backing, the abscissa is contrast ratio, $C_{R'}$. Figure 1 is a reflectance-opacity chart in which the abscissa is $C_{0.89}$ or TAPPI opacity.[4] Figure 2 is a reflectance-opacity chart in which the abscissa is $C_{0.80}$. Figure 3 is a chart in which the abscissa is $C_{0.70}$. The curves having positive slopes represent the increase in reflectance and opacity of specimens made of increasing thicknesses of the same ideal material. The highest reflectance is obtained, of course, for specimens so thick that they are opaque ($C_{R'}=1.00$), and this maximum reflectance is the reflectivity, R_∞. The relative thicknesses of the specimens are indicated by the intersections with the curves having negative slopes. Each of the latter curves represents ideal specimens of constant scattering power, SX; each such curve shows the decrease in reflectance, R_0, for black backing and the increase in opacity, $C_{R'}$, of such specimens as their reflectivities are lowered as, for example, by admixture of a non-scattering, light-absorbing material like black dye or black pigment.

These charts[5] provide solutions for the two constants R_∞ and S, of the ideal material from thickness of sample and given values of measurable reflectances, R_0 and $R_{R'}$. Or, if R_∞ is determined by direct reflectance measurement of a thick layer, the charts yield scattering coefficient, S, from thickness of sample, X, and reflectance, R_0. In the present work, these relations were investigated by means of values of A_0, A_∞, and $A_{R'}$, the analogues of R_0, R_∞, and $R_{R'}$. Figure 1 is particularly applicable to measurements of paper because its abscissa is $C_{0.89}$, the particular contrast ratio identified with opacity according to the test methods of the Technical Association of the

[4] D. B. Judd, *The dependence of reflectance and opacity on thickness; Relation between contrast ratio and printing opacity*, Paper Trade J. **101**, no. 5, TS 40 (August 1, 1935).

[5] A chart serving similar purposes, but having transmission as abscissa instead of opacity, was worked out by Gurevich. (See footnote 1.)



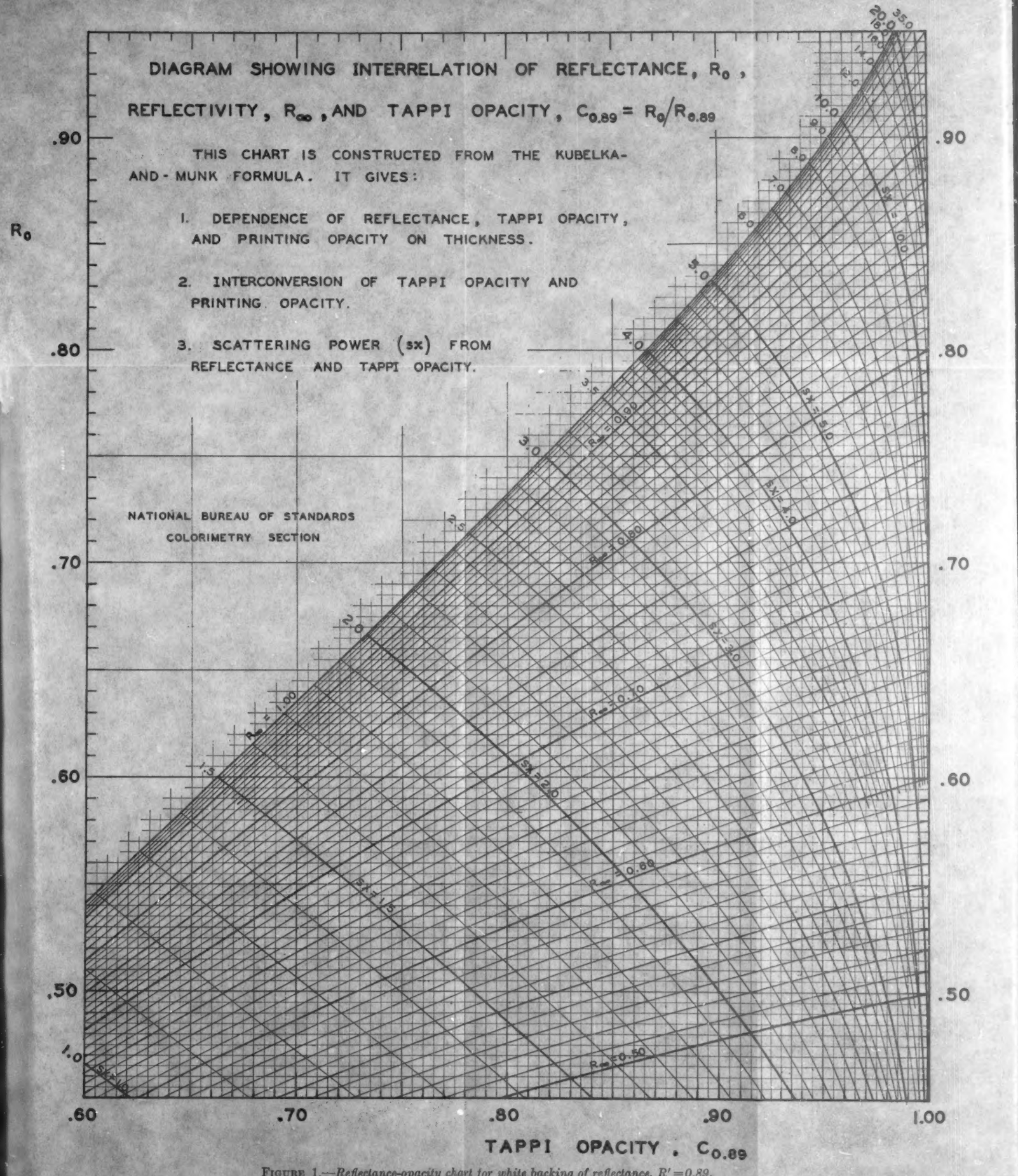


FIGURE 1.—*Reflectance-opacity chart for white backing of reflectance, $R' = 0.89$.*

To be used in specification of paper.

7187—37 (Face p. 290, RP1026) No. 1

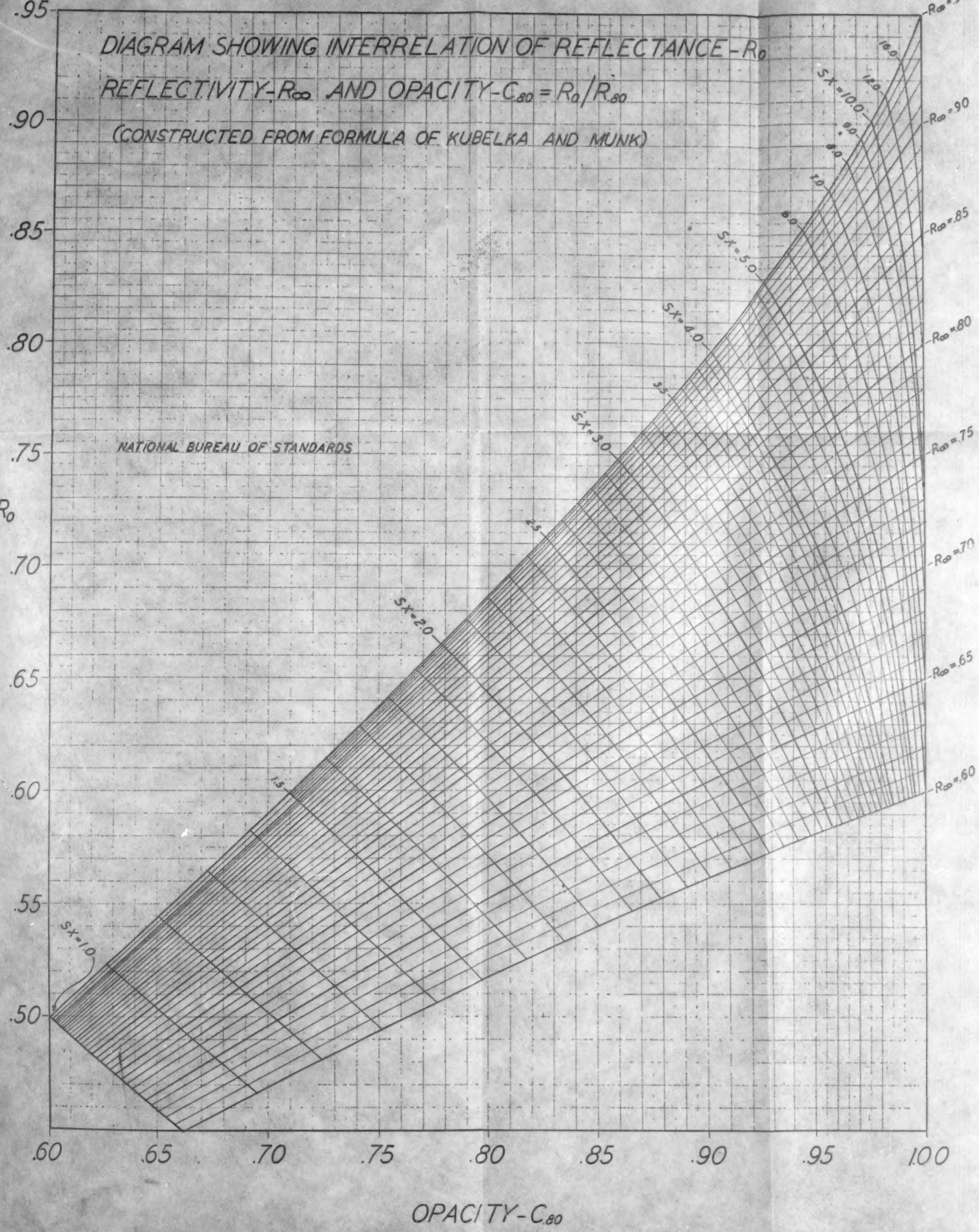


FIGURE 2.—*Reflectance-opacity chart for white backing of reflectance, R' = 0.80.*

To be used in specifiention of vitreous enamels and paints.

7187—37 (Face p. 290, RP1026) No. 2

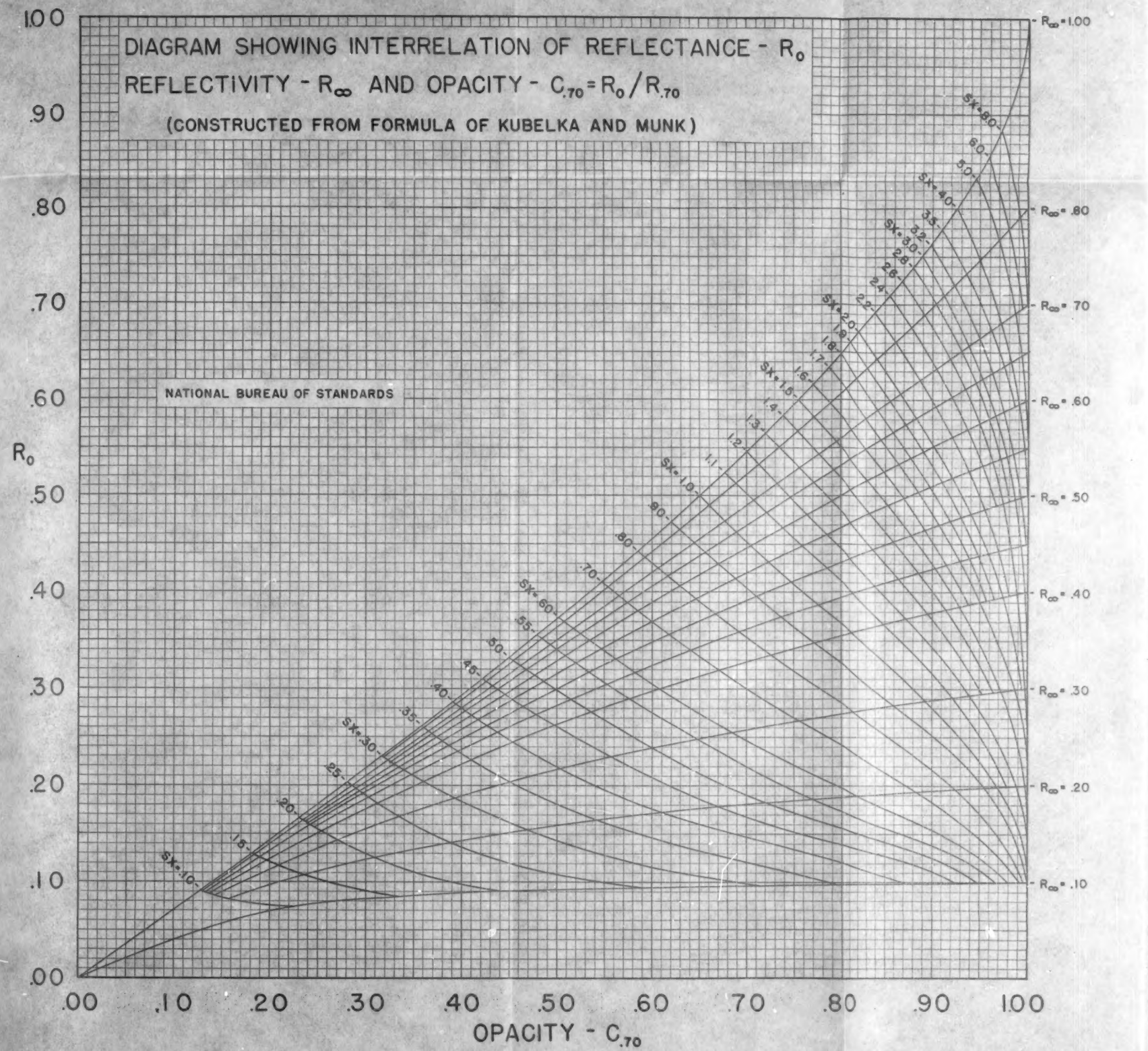


FIGURE 3.—*Reflectance-opacity chart for white backing of reflectance, R' = 0.70.*

To be used in specification of dental silicate cements.

7187—37 (Face p. 290, RP1926) No. 3

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Pulp and Paper Industry.[6] Figure 2 refers more particularly to vitreous enamels and paint films because it is more feasible to use as the white backings in such cases coatings which have a reflectance of about 0.80. Figure 3 is used here for dental silicate cements because white backings having reflectances of about 0.70 were found to be convenient for this material.

In many cases, it was found that the white backing did not exactly equal either 0.70, 0.80, or 0.89, so none of the charts could be used directly. In such cases use was made of a formula connecting contrast ratio, $C_{R'}$ with R', R_0, and ideal contrast ratio, C.[7] This formula is also based on the assumption that the illumination of the specimen is perfectly diffused, but applies to nonhomogeneous as well as homogeneous specimens. It is particularly convenient in the reduction of various kinds of data because R', C, and $C_{R'}$ may each be found explicitly, thus:

$$C_{R'}=\frac{C(1-R'R_0)}{C(1-R')+R'(1-R_0)} \tag{2a}$$

$$C=\frac{R'C_{R'}(1-R_0)}{1+R'C_{R'}-C_{R'}-R'R_0} \tag{2b}$$

$$R'=\frac{C(1-C_{R'})}{C_{R'}(1-C)+R_0(C-C_{R'})} \tag{2c}$$

By substituting equation 2b in equation 2a, an expression for $C_{R'}$ may be found for any desired value of R', say 0.89, provided R_0 and $C_{R'}$ for any other value of R' be known. This expression is written for $R'=0.89$, $R'=0.80$, and $R'=0.70$, respectively:

$$C_{0.89}=\frac{1-0.89R_0}{0.11+\dfrac{0.89(1-R'R_0-C_{R'}+R'C_{R'})}{R'C_{R'}}} \tag{3a}$$

$$C_{0.80}=\frac{1-0.80R_0}{0.20+\dfrac{0.80(1-R'R_0-C_{R'}+R'C_{R'})}{R'C_{R'}}} \tag{3b}$$

$$C_{0.70}=\frac{1-0.70R_0}{0.30+\dfrac{0.70(1-R'R_0-C_{R'}+R'C_{R'})}{R'C_{R'}}} \tag{3c}$$

If R_0 and $C_{R'}$ ($R'\neq 0.89$) be measured for a given specimen and it be desired to use figure 1 for finding the constants R_∞ and S of the material of this specimen, equation 3a may be used. If it be desired to use fig. 2 or 3 for finding the constants of the material, equation 3b or 3c, respectively, may be used. Figure 4 is based on equation 3b and shows how the correction, $C_{R'}-C_{0.80}$, varies with $R'-0.80$ for different values of $C_{0.80}$ and R_0. Note that the correction in every case is so nearly proportional to $R'-0.80$ that for deviations of R' from 0.80 equal to 0.01 no significant errors (errors greater than 0.002) will occur if the correction is computed as one-tenth of that for

[6] See footnote 3. The apparent reflectance of white backing mentioned in the standard method is 0.915 relative to that for magnesium oxide. Since the reflectance of magnesium oxide for diffuse illumination is about 0.97, this corresponds to $R'=0.915\times 0.97=0.89$.

[7] D. B. Judd, *Opacity standards*, J. Research NBS **13**, 281 (1934) RP709; Paper Trade J. **100**, no. 1, TS 28 (1935).

$|R'-0.80|=0.10$. Figures 5 and 6 were computed from equations 3b and 3c, respectively, and, by virtue of the near proportionality between correction and deviation of R' from the plotted value (0.80, 0.80, or 0.70), as in figure 4, figures 5 and 6 serve the purposes of equations 3a, 3b, and 3c for most cases arising in practice. The dotted curves (constant R_∞) on these figures were found by reference

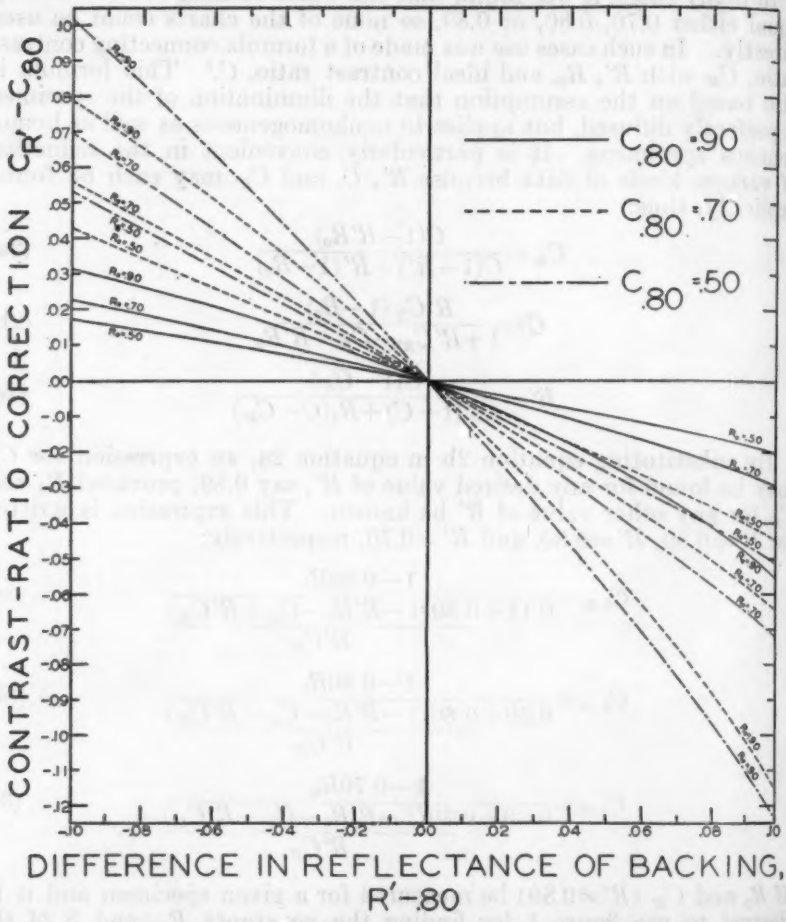

FIGURE 4.—*Demonstration that the correction to contrast-ratio is nearly proportional to change in reflectance of white backing, R'.*

to the respective reflectance-opacity charts (figs. 1, 2, and 3), and are often more convenient for obtaining interpolated values than the solid curves (constant R_0).

3. CONDITIONS OF MEASUREMENT

The general plan in this investigation has been to use the reflectometers customarily applied to the materials investigated, and to use them in the customary ways. Some of the usual methods, however, are such that no close check on the Kubelka-Munk formula is to be expected, and such methods have been avoided. It is convenient in

the discussion of these methods to classify the materials investigated as (1) those in which the scattering elements are distributed in air as

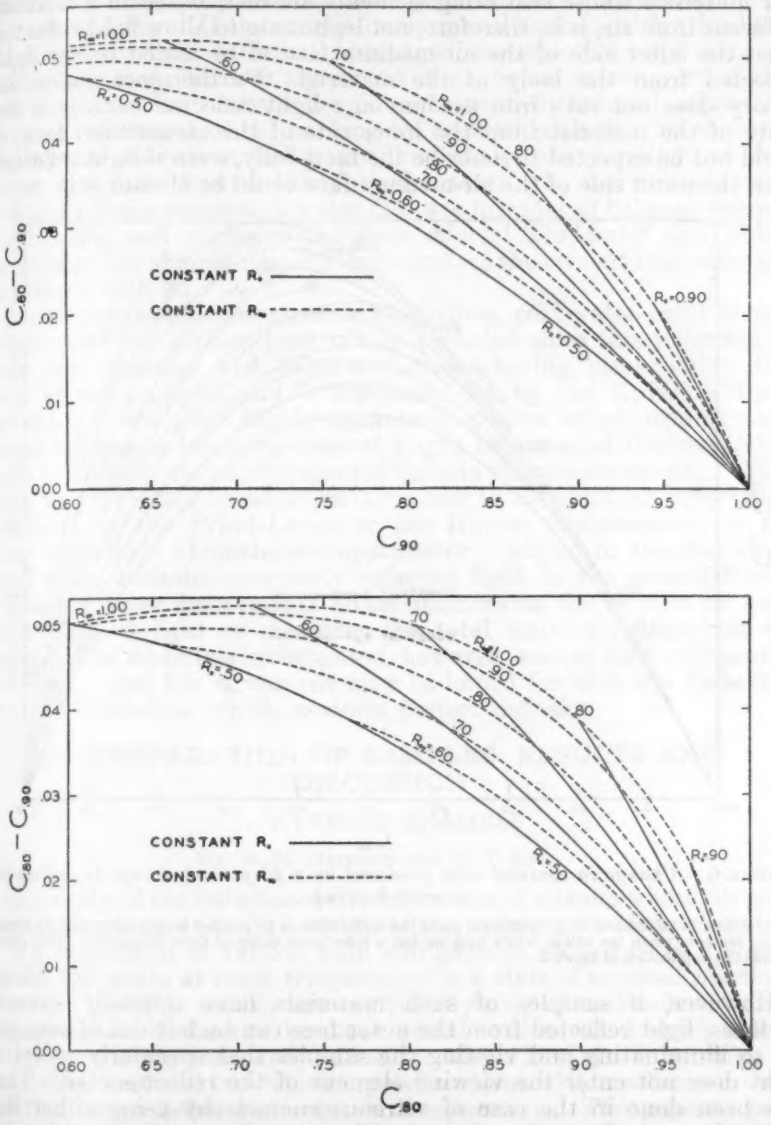

FIGURE 5.—*Change in contrast-ratio produced by a 10-percent change in reflectance of white backing.*

To be used (upper graph) in estimating by proportional parts the corrections to be applied to contrast ratios for paper when the actual white backing has a reflectance different from 89 percent, also (lower graph) for vitreous enamels and paints when the actual white backing has a reflectance different from 80 percent. This graph extends the application of figures 1 and 2.

the medium (uncoated papers, cold-water-paint films), and (2) those in which the medium is not air (vitreous enamels, dental silicate cements).

The pertinence of this classification lies in the assumption by Kubelka and Munk that the hypothetical material is homogeneous. For materials whose scattering elements are distributed in a medium different from air, it is, therefore, not legitimate to allow light reflected from the outer side of the air-medium face to be added to the light reflected from the body of the material. Furthermore, since the theory does not take into account any light reflected back into the body of the material from the inner side of the air-medium face, it could not be expected to describe the facts fully, even if light reflected from the outer side of the air-medium face could be eliminated.

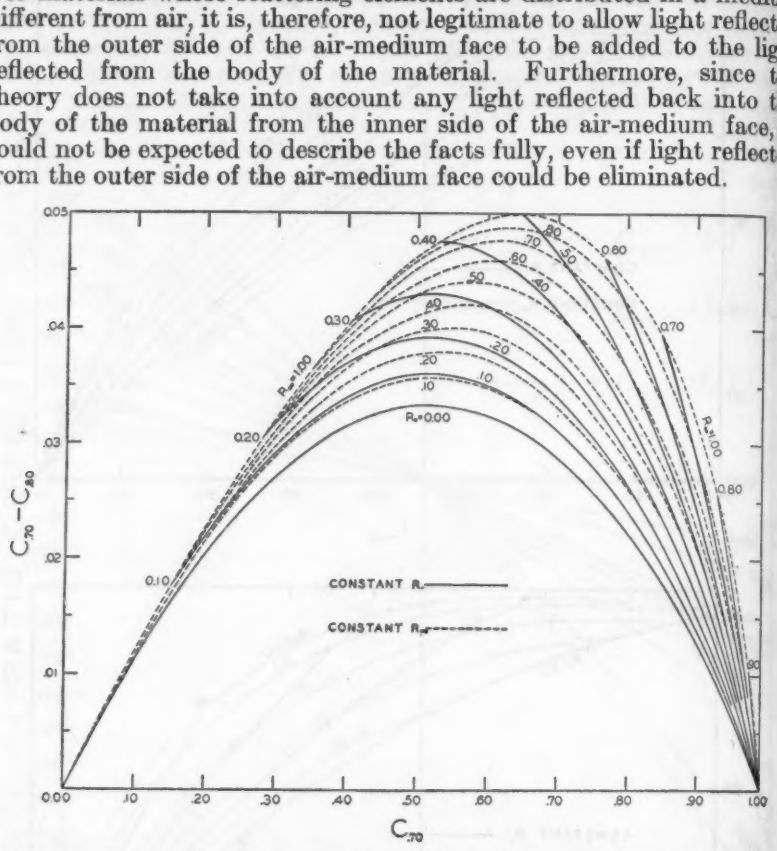

FIGURE 6.—*Change in contrast-ratio produced by a 10-percent change in reflectance of white backing.*

To be used in estimating by proportional parts the corrections to be applied to contrast ratios for dental silicate cements when the actual white backing has a reflectance different from 70 percent. This graph extends the application of figure 3.

However, if samples of such materials have optically smooth surfaces, light reflected from the outer face can be left out of account by so illuminating and viewing the samples that specularly reflected light does not enter the viewing element of the reflectometer. This has been done in the case of vitreous enamels by using either the Priest-Lange reflectometer [8] or the Hunter reflectometer in either its visual [9] or photoelectric [10] form. The specimens of dental silicate cement do not have optically smooth surfaces, however, and in this case the effect of first-surface reflection was largely avoided by covering the sample with a film of water.

[8] I. G. Priest, *The Priest-Lange reflectometer applied to nearly white porcelain enamels*, J. Research NBS **15**, 529 (1935) RP847.

[9] R. S. Hunter, *A reflectometer and color comparator*, Sci. Sec. Cir. C461, National Paint, Varnish, and Lacquer Assn., Washington, D. C. (April 1934).

[10] R. S. Hunter, *A null method photoelectric reflectometer*, J. Opt. Soc. Am. **26**, 225 (1936); Bul. Am. Ceramic Soc. **15**, 79 (1936); Better Enameling **7**, 12 (March 1936).

Similar considerations govern determinations of the effective reflectance of the backing, although their neglect may be expected to introduce considerably smaller discrepancies except for specimens of very low opacity. If the sample be in optical contact with a backing which absorbs light sufficiently strongly, the effective reflectance of the backing may, without significant error, be set at zero, but if the optical contact be broken, the film of air so introduced raises the effective reflectance of the backing by as much as 0.12. In the case of vitreous enamels and oil paint films, the ordinary method of preparing specimens insures this optical contact. In our measurement of dental silicate cements, a water film was introduced between sample and backing and produced the same effect. The water film which surrounded the sample served also to protect the cement from changes by contact with air.

For materials whose medium is air (papers, cold-water-paint films), reflection at the surface need not be excluded since this reflection is quite homogeneous with other reflections taking place within the body of the material and is accounted for by the Kubelka-Munk formula. Indeed, for highly calendered papers which exhibit considerable gloss, a better agreement might be expected if provision is made to include specularly reflected light in the measurements. This could be done either by adding a correction to the apparent reflectance measured by the Priest-Lange or the Hunter reflectometer, or by using the Davis photoelectric opacimeter [11] which, in the manufactured form, includes specularly reflected light in the measurement.

None of these instruments either illuminates the sample by perfectly diffused light or measures the total amount reflected at all angles. The materials investigated, however, scatter light sufficiently completely that fair agreement may be hoped for with the Kubelka-Munk formulation, which assumes perfect diffusion.

IV. PREPARATION OF SAMPLES: RESULTS AND DISCUSSION

1. VITREOUS ENAMELS

By W. N. Harrison and B. J. Sweo

In a study of the reflectance characteristics of opaque white vitreous enamel, cognizance should be taken of the constitution of the material. It is a suspension of various solid and gaseous occlusions in a glassy matrix and exists at room temperature in a state of arrested reaction. The solid particles usually are composed partly of undissolved materials contained in the raw batch or added to the fritted batch before grinding, or both, and partly of matter which has been in solution in the molten material but which crystallized out within a limited temperature range below the solution temperature. The gaseous particles are probably partly occluded air and partly products of reaction between the materials used (including the metal base), and of volatilization.

At and near room temperature the progress toward equilibrium between the components is ordinarily imperceptible, but above 500 to 600°C the rates of reaction between the constituents probably increase rapidly with temperature, as does the fluidity of the suspending medium.

[11] M. N. Davis, *A simple and reliable photoelectric opacity tester*, Tech. Assn. Pap. [16], 277 (1933).

These facts are important, especially because in applying enamel to metal the powdered-enamel coating is fired at temperatures varying approximately from 700 to 950°C, depending on the composition, and at such temperatures these reactions and consequent modification of characteristics proceed, though naturally at slower rates than those which prevail when the raw batch is originally "smelted" to form the frit at temperatures several hundred degrees higher. While this comparative slowness of reaction at firing temperatures, and the brevity of exposure (only a few minutes are required for small pieces), combine to repress changes in characteristics during firing, the fact cannot

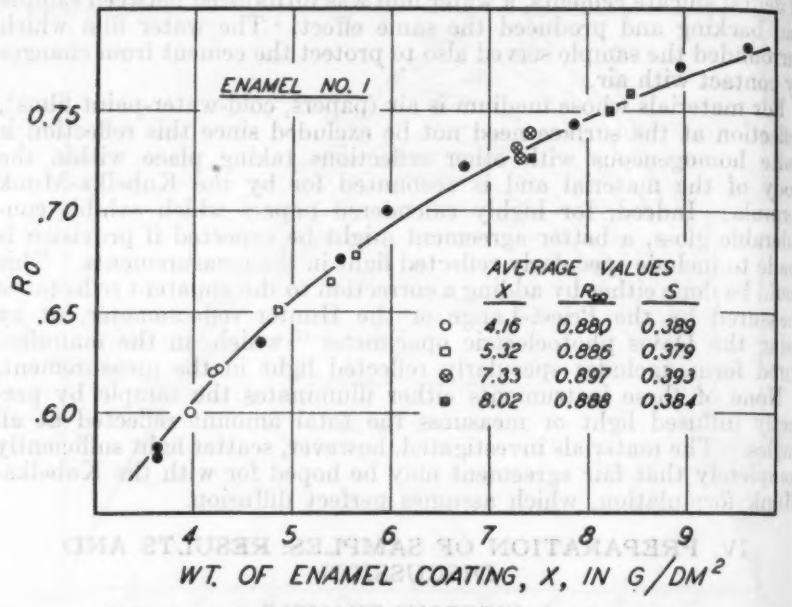

FIGURE 7.—*Constants determined by contrast-ratio method.*

Four determinations were made from the respective averages of four sets of three specimens each. The values of R_0 for these specimens are shown as circles, squares, crossed circles, and crossed squares, respectively, and the constants for each determination are shown. The solid circles represent determinations of weight of coating versus reflectance which were independent of the contrast-ratio specimens. The curve was plotted from the average values of the respective constants.

be overlooked that changes of this type, and also some degree of interpenetration between a white cover coat and a black undercoat, do occur.

The purpose of the work on enamels was to determine whether, in spite of their heterogeneity and comparative instability at firing temperatures, the relations between apparent reflectance and thickness within practical limits could be satisfactorily expressed in terms of the Kubelka-Munk constants on the assumption that apparent reflectance, A, gives an adequate evaluation of reflectance, R. In accord with the assumption, the determined values of A are hereinafter referred to as R.

It soon became evident that the inspection areas covered by most reflectometers (usually 6 cm² or less) are not large enough to be representative of specimens 1 dm square having thin coatings of low opacity because such coatings are generally not sufficiently uniform. Since

for practical reasons it is not feasible to reduce the size of enameled specimens drastically below 1 dm², a reflectometer covering a large fraction of this area was desired, and the Hunter Photox photo-electric reflectometer was selected. The instrument used covers an inspection area which is nearly circular and about 7 cm in diameter.

(a) CONTRAST-RATIO METHOD

The first method of study was to determine the contrast ratio ($C_{0.80}$) and from this value, together with the reflectance (R_0) of coatings of known weight per unit area (X) over black backing, to estimate the constants, reflectivity (R_∞) and coefficient of scatter (S), by means of the chart shown in figure 2. This method involved the preparation of test blanks with a black enamel on one-half and a white enamel of reflectance 0.80 on the other half.[12]

Figure 7 is representative of the more favorable results obtained by this method. The data corresponding to this figure, which were obtained from highly opaque enamel frit with no opacifier added at the mill, are given in table 1.

TABLE 1.—*Reflectance data for enamel 1, contrast-ratio method*

Reflectance of backing, R'	Weight of enamel, X	Reflectance of coating over—		$R_0/R_{0.8}' \equiv C_{0.8}'$	Opacity, $C_{0.80}$	Scattering power, SX	Coefficient of scatter, S	Reflectivity, R_∞
		Black backing, R_0	White backing, $R_{0.8}'$					
	g/dm²							
0.814	3.99	0.599	0.840					
.825	4.22	.616	.846					
.812	4.27	.618	.840					
Average	.817	4.16	.612	.842	0.727	0.785	1.62	0.389	0.880
.810	4.88	.650	.842					
.813	5.41	.664	.849					
.815	5.66	.678	.850					
Average	.813	5.32	.664	.847	.784	.790	2.04	.379	.886
.816	7.31	.726	.858					
.816	7.27	.732	.859					
.807	7.41	.739	.859					
Average	.813	7.33	.732	.859	.852	.857	2.88	.393	.897
.812	7.43	.726	.856					
.809	8.22	.749	.859					
.815	8.41	.758	.860					
Average	.812	8.02	.744	.858	.867	.872	3.09	.384	.888

The constants R_∞ and S were computed four times, from four groups of three specimens each, at different average thicknesses of the test coating. The R_0 values of these contrast-ratio specimens are shown in figure 7 as circles, squares, crossed circles, and crossed squares, respectively. The solid circles represent independently determined points, obtained from coatings over ordinary black-coated blanks, rather than contrast-ratio blanks.

It is seen that the four pairs of independently determined constants agree reasonably well with each other, and that all the experi-

[12] The white and black backings could be used on separate specimens, but this procedure would involve the comparison of pairs of specimens with equal coatings of test enamel.

mental points fall close to the theoretical line corresponding to the average value of the two constants.

Such fairly consistent results were not, however, obtained without close attention to numerous details, and even then not in all cases. This fact is probably due in part to sources of error peculiar to this method of test. Known deviations from 0.80 in the reflectance of the white backing were corrected for by means of figure 5, but any change in reflectance of the backing which might occur during the firing of the test coating could not be similarly corrected for, since both its direction and extent were unknown. Also, errors in reflectance measurements may be accentuated in the ratio of two reflectance measurements, from which the contrast ratio was determined. Further, the assumption that the enamel is applied in equal thicknesses to both ends of the specimen, although this condition was sought, is subject to more or less error, depending on the skill of the operator. Less opaque enamels appeared to be more affected by the sources of error, since in general results for them were less satisfactory.

No data in addition to table 1 and figure 7 are given for the contrast-ratio method, since the data obtained were largely of a preliminary nature and not suitable for drawing definite conclusions. Rather than make a more exhaustive study of this method, and the perfection of a dependable technique applicable to all classes of white enamel, the following method was investigated, which it was hoped would be less dependent upon carefully controlled technique and specialized skill for satisfactory reproducibility.

(b) REFLECTIVITY METHOD

(1) *Technique.*—In this method the reflectivity was determined by direct measurement of the reflectance of a thick coating. The thickness required may be seen from figure 2 to correspond to scattering powers (SX) of 16 for reflectivities up to 0.85; and even for reflectivity 0.90, the reflectance R_0 for this scattering power differs from the reflectivity by only 0.005. Preliminary data indicated that suitable scattering powers could be obtained by coatings of 75g/dm^2.

Although reflectances of these heavy coatings cannot be used alone to obtain coefficients of scatter, they may be used for this purpose when combined with reflectance data for the thinner coatings encountered in commercial practice for wet-process enamels (4 to 9 g/dm^2, dry weight). Ordinarily one specimen was coated at about 4 g/dm^2, one at about 4½, and so on by approximately ½-g increments to 9 g/dm^2, each dried coating being weighed by difference to the nearest 0.01 g. However, for enamels having very low covering power, P, it was found advisable to use somewhat greater thicknesses.

To keep the firing practice as uniform as possible, the specimens in this range of thickness were fired in a single firing period (for the cover coat). The heavier coats were applied in two (or if necessary three) sprayings, any spray coat subsequent to the first being kept dry enough by adjustment of the spray gun to prevent its glossing over during spraying. (Without this precaution the application of two or more spray coats before firing was not uniformly successful.) The specimens coated with 75 g/dm^2 of enamel could be prepared in the same fashion, by spraying on numerous coats to be fired at once, but although this process was tried successfully, it was considered

more practicable to dry out the enamel suspension known as "slip" and apply the powder by the dry process.

(2) *Results.*—Three enamels were tested by the reflectivity method; one enamel of high covering power, P, one low and one interme-

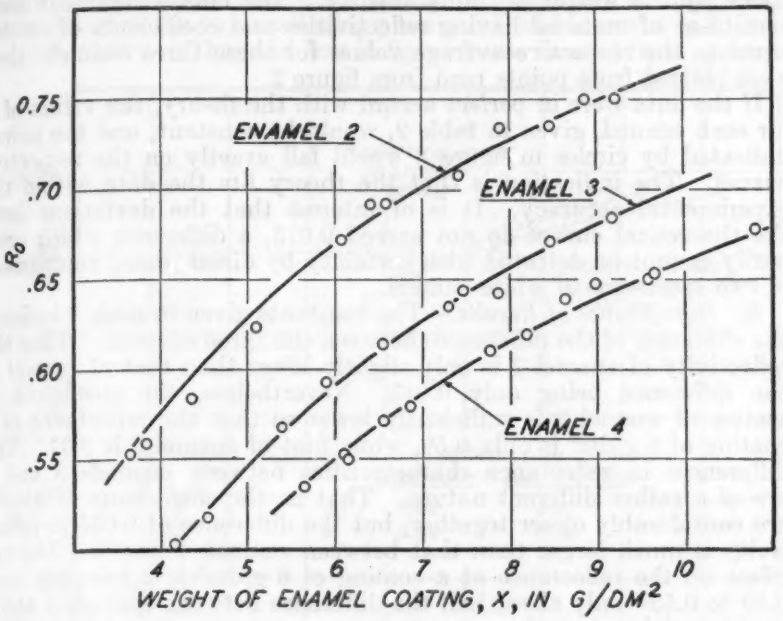

FIGURE 8.—*Constants determined by direct observation of reflectivity and use of the observed value R_∞, with plotted values of R_0 to read coefficient of scatter from figure 2.*

diate. All were given equal grinding treatment with 7 parts by weight of clay for each 100 parts of frit, and no opacifier was added at the mill. The results are shown in table 2 and figure 8.

TABLE 2.—*Reflectance data for enamels 2, 3, and 4, reflectivity method*

Enamel 2 [a]				Enamel 3 [b]				Enamel 4 [c]			
X	R_0	SX	S	X	R_0	SX	S	X	R_0	SX	S
g/dm²				g/dm²				g/dm²			
3.65	0.553	1.25	0.342	4.16	0.501	1.02	0.245	5.65	0.536	1.21	0.214
3.83	.559	1.28	.334	4.53	.518	1.09	.241	6.10	.552	1.29	.212
4.35	.584	1.43	.329	5.40	.567	1.33	.246	6.12	.551	1.29	.211
5.08	.624	1.69	.333	5.87	.594	1.50	.255	6.55	.572	1.41	.215
6.06	.673	2.12	.350	6.55	.616	1.64	.250	6.85	.580	1.46	.213
6.40	.692	2.32	.362	7.30	.635	1.79	.245	7.78	.611	1.68	.216
6.58	.693	2.34	.356	7.49	.644	1.87	.250	8.21	.619	1.74	.212
7.42	.708	2.52	.340	7.88	.643	1.86	.236	8.65	.639	1.92	.223
7.88	.734	2.89	.367	8.47	.672	2.12	.250	8.99	.648	2.01	.224
8.46	.736	2.92	.345	9.18	.686	2.28	.249	9.60	.650	2.02	.210
8.87	.750	3.16	.356					9.64	.653	2.07	.215
9.22	.751	3.18	.345					10.81	.678	2.35	.217
Average			0.348				0.247				0.215

[a] R_∞=0.901, 0.897; average 0.899.
[b] R_∞=0.884, 0.887; average 0.886.
[c] R_∞=0.824, 0.818; average 0.821.

From the average values of R_∞, and the observed values of R_0 for the respective specimens in the weight-reflectance series, the scattering power, SX, for each such specimen was read from figure 2, and the coefficient of scatter, S, was computed in each case by dividing this figure by the weight per unit area, X. The curves represent ideal specimens of material having reflectivities and coefficients of scatter equal to the respective average values for these three enamels; they were plotted from points read from figure 2.

If the data were in perfect accord with the theory, the values of S for each enamel, given in table 2, would be constant, and the points indicated by circles in figure 8 would fall exactly on the respective curves. The indication is that the theory fits the data within the experimental accuracy. It is of interest that the deviations from the theoretical curves do not exceed 0.013, a difference which ordinarily cannot be detected with certainty by direct visual comparison of two specimens of white enamel.

(3) *Significance of Results.*—The constants given in table 2 indicate the character of the differences between the three enamels. Thus the reflectivity of enamel 3 is only slightly lower than that of enamel 2, the difference being only 0.013. Nevertheless, the coefficient of scatter of enamel 3 is sufficiently lower so that the reflectance of a coating of 6 g/dm² is only 0.59, while that of enamel 2 is 0.67. The differences in reflectance characteristics between enamels 3 and 4 are of a rather different nature. That is, the coefficients of scatter are considerably closer together, but the difference of 0.065 in reflectivity is much larger than that between enamels 2 and 3. The net effect on the reflectance at a coating of 6 g/dm² is a lowering from 0.59 to 0.55—only about half the difference between enamels 2 and 3 at this weight of coating.

The constants may also be used in connection with figure 2 to determine the covering power, P, of each enamel. These values are nearly 0.79, 0.71, and 0.68 for enamels 2, 3, and 4, respectively. By comparing these values with the average constants in table 2, it is seen that the changes in covering power, P, follow the changes in coefficient of scatter, S, much more closely than they do the changes in reflectivity, R_∞, of these three typical "white" enamels.

(c) DUAL-THICKNESS METHOD

The procedure used in these tests was (a) to obtain a reflectance, R_0, for a wet-process coating of about 18 g/dm² from the average observed reflectance of two specimens having that weight of coating, and (b) in the lower-weight range, to determine the reflectance for a coating of one-third the above-stated thickness by interpolation from a set of specimens prepared as previously described. The constants were determined from figure 2, as illustrated by the following case, the data for which are shown in figure 9. The average coating of the two most heavily coated specimens was 17.85 g/dm² and the average reflectance was 0.833. The reflectance corresponding to 5.95 g/dm² (one-third of 17.85 g/dm²) was read by interpolation on a smooth curve closely representing the data between 4 and 9 g/dm² and found to be 0.687. The problem was, then, to find a constant-reflectivity line on figure 2 such that the scattering power, SX, at a reflectance of 0.833 is three times the scattering power at a reflectance of 0.687.

It was found by inspection that the line for $R_\infty=0.87$ approximately meets this condition. The ratio of the scattering powers is 2.94 for $R_\infty=0.87$ and 3.15 for $R_\infty=0.86$, and by interpolation the ratio is equal to 3.0 when $R_\infty=0.867$, which is, therefore, the reflectivity sought.[13] The coefficient of scatter, S, was found by dividing out X from either of the two scattering powers SX which served to identify the reflectivity. The solid line in figure 9 was located from constants

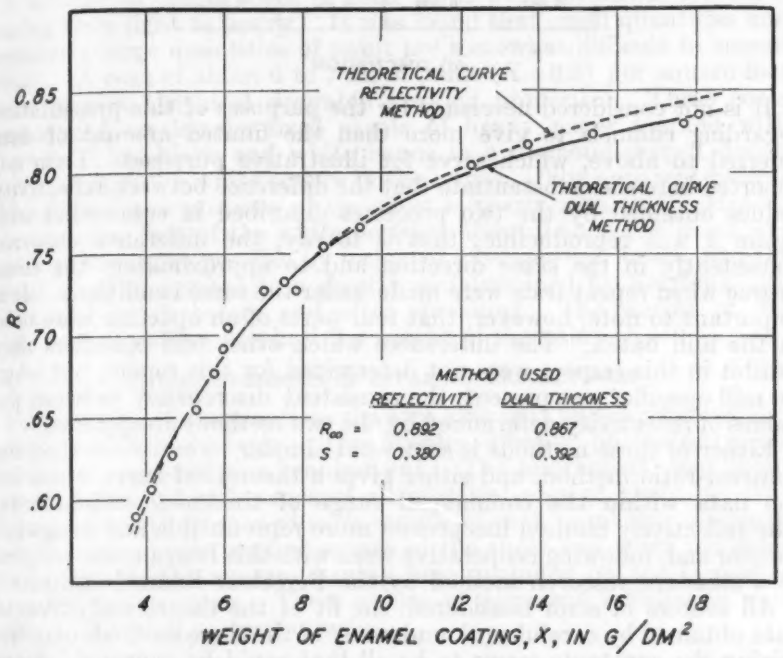

FIGURE 9.—*Continuous line corresponds to constants determined by the dual-thickness method, dotted line to constants determined by reflectivity method.*

determined in this fashion. The points between 12 and 16 g/dm² represent supplementary check values, and were not used in determining the constants.

For comparison the reflectivity was also observed directly, as previously described, from specimens coated by dry process with 75 g/dm² of this enamel. The observed value was 0.892, which is 0.025 greater than that computed from the wet-process data. The dotted line in figure 9 was drawn from this value of R_∞ and the value of S computed by figure 2 from it and from the same point on the weight-reflectance curve used before, namely, $X=5.93$ and $R_0=0.687$. The constants obtained by the two methods are given in table 3.

It is seen from figure 9 that the curve obtained by either method fits the observed points in the commercial range 4 to 9 g/dm² within experimental accuracy, and that above this range some points are closer to one curve and some to the other.

[13] A set of curves giving a rapid explicit solution for reflectivity, to replace the trial and error solution by means of figure 2, could be prepared and should be available if this method were to be used regularly.

TABLE 3.—*Medium-opacity enamel*

[Four parts opacifier *A* added at the mill]

Reflectivity method		Dual-thickness method	
R_∞	S	R_∞	S
0.892	0.380	0.867	0.392

(d) DISCUSSION

It is not considered necessary for the purposes of this presentation regarding enamels to give more than the limited amount of data referred to above, which serve for illustrative purposes. Data not reported here also substantiate that the difference between reflectivity values obtained by the two processes described in connection with figure 9 was reproducible; that is to say, the difference occurred consistently in the same direction and to approximately the same degree when repeat tests were made under the same conditions. It is important to note, however, that four parts of an opacifier were used in the mill batch. The differences which other mill opacifiers may exhibit in this respect were not determined for this report, but when no mill opacifier was present, the consistent discrepancy between the values of reflectivity determined by the two methods disappeared.

Either of these methods is somewhat simpler to carry out than the contrast-ratio method, and either gives a theoretical curve which fits the data within the commercial range of thickness satisfactorily. The reflectivity method has proven more reproducible and somewhat simpler and, following cooperative work with this Bureau, was adopted as a standard research method by the Porcelain Enamel Institute.[14]

All sources of error considered, the fit of the theoretical curves to data obtained by careful work under any of the three methods of determining the constants seems to be all that could be expected. Since each of the two Kubelka-Munk constants has a physical significance, as revealed in the respective definitions, the results give a basis of comparing different enamels and mill batches, and determining the character of effects produced by given changes in enamels or mill batches, which offers much promise of usefulness in the field of vitreous enamels.

2. COLD-WATER PAINTS

By E. F. Hickson and A. J. Eickhoff

Cold-water paints may be described as a mixture of materials with some water-soluble vehicle (casein, glue, etc.). Water acts merely as a thinner or solvent necessary for purposes of application. Thus, after drying, the film is essentially a pigment with air as the medium.

This work was undertaken to determine whether or not the fundamental optical properties of a dry cold-water paint film followed the equations of Kubelka and Munk.

[14] Reflectance Test for Opaque White Porcelain Enamels, obtainable from the Porcelain Enamel Institute, 612 N. Michigan Ave., Chicago, Ill.

(a) PREPARATION OF SAMPLES

The cold-water paints studied are supplied in the form of a paste. The fraction, K, by weight of dry solids in each paste was first determined; then a paint was made from each paste by adding water until the weight of dry solids was equal to that of the water in the paint ($K=0.5$). The density, D, of this paint was then determined by weighing a known volume of it.

A number of single coats of each paint were prepared, the coats ranging from light to heavy. It was found that small quantities and excessively large quantities of paint are somewhat difficult to spread evenly. A coat of about 6 to 7 ml of paint ($K=0.5$) per square foot seems to give the most desirable working properties. These coats were spread on lacquer-sized sheets of heavy paper marked with alternate ½ in. black and white bands in a diamond-shaped design with a black and a white square in the center. The apparent reflectance of the black portions of the sheet is nearly zero on the Hunter reflectometer, that of the white portions about 0.80. The paint was spread as evenly as possible by means of a badger-hair brush, and the weight of paint applied to a sheet was determined by weighing container and brush before and after spreading. The weight of dry solids was, of course, one-half the weight of the paint ($K=0.5$).

(b) MEASUREMENTS OF APPARENT REFLECTANCE

For purposes of examination, the area averaged by the reflectometer should be relatively large. The Hunter Photox photoelectric reflectometer answered this requirement. The instrument used measures the apparent reflectance of an elliptical area of about 40 cm². The apparent reflectance of each sample of each paint was measured both from the white central square of the sheet and from the black central square, the squares having been included on the lacquered sheet for this purpose. These values of apparent reflectance were taken as R_0 and $R_{0.80}$, respectively.

(c) REDUCTION OF DATA

Tables 4, 5, and 6 give detailed data for two paints, *a* and *c*; and table 7 gives a summary for the nine paints studied. Table 5 gives results of repeat measurements on the same paint (*a*) dealt with in table 4; it indicates the experimental uncertainty of the reflectance measurements, most of which is ascribable to difficulty of applying the paint evenly. Contrast ratio, $C_{0.80}$, was computed as $R_0/R_{0.80}$. The reflectivity, R_∞, and scattering power, SX, were read from the reflectance-opacity chart (fig. 2). It is not possible to obtain a reliable measurement of the thickness, X, of the dry paint films, nor is such a measurement of very great interest. The thickness, X, has been expressed in three ways: first, as the thickness of the wet coat, in microns; second, as the weight per unit area of dry solids, g/ft²; and third, as the volume of original paste per unit area, ml/ft². The thickness of the wet film in microns has been used as an approximation to the thickness of the dry paint films for the purpose of comparing the properties of cold-water-paint films with other scattering materials, see section V. If the paint were supplied, as many cold-water paints are, in the form of a dry powder sold by weight, the most useful measure of thickness of the coat would be weight, M, of dry solids per unit area; but since these paints were supplied in the form of paste

sold by volume, the measure of thickness, X, used is volume, V, of original paste per unit area. This volume, V, is computed from the fraction, K, by weight of dry solids in the original paste, and the density, D, of the paint made up so that $K=0.5$ according to the readily derived relation:

$$V=M\,[(1-K)/K+2/D-1] \tag{4}$$

TABLE 4.—*Detailed data for paint a2*

Weight, M, of dry solids	Reflectance on black R_0	Reflectance on white $R_{0.80}$	Contrast ratio black/white $C_{0.80}$	Volume, V, of paste	R_∞	SX	S (X in ml/ft.²)
[a] g/ft.²				ml/ft.²			
2.52	0.785	0.870	0.902	2.04	0.912	3.85	1.9
2.77	.765	.870	.880	2.25	.923	3.35	1.5
2.97	.760	.870	.874	2.41	.930	3.24	1.3
3.92	.770	.855	.900	3.18	.907	3.52	1.1
3.94	.830	.880	.944	3.19	.906	5.50	1.7
4.28	.840	.880	.955	3.47	.900	6.2	1.8
5.08	.850	.890	.955	4.12	.916	6.3	1.5
5.49	.845	.885	.955	4.45	.908	6.3	1.4
5.79	.855	.895	.955	4.69	.925	6.5	1.4
6.02	.865	.900	.961	4.88	.930	7.0	1.4
Average					0.916		1.50

[a] These hybrid units are widely used by paint technologists. The more rational units, grams per square decimeter and milliliters per square decimeter, have on this account not been used here.

TABLE 5.—*Detailed data for paint a1*

Weight, M, of dry solids	Reflectance on black R_0	Reflectance on white $R_{0.80}$	Contrast ratio black/white $C_{0.80}$	Volume, V, of paste	R_∞	SX	S (X in ml/ft.²)
g/ft.²				ml/ft.²			
2.86	0.770	0.875	0.880	2.32	0.940	3.40	1.5
3.26	.790	.880	.898	2.64	.940	3.85	1.5
3.39	.790	.870	.908	2.75	.908	4.07	1.5
3.92	.820	.880	.932	3.18	.912	4.97	1.6
4.29	.810	.880	.920	3.48	.923	4.48	1.3
4.34	.830	.885	.938	3.52	.920	5.30	1.5
4.92	.845	.890	.950	3.99	.920	6.00	1.5
5.17	.845	.890	.950	4.19	.920	6.00	1.4
5.74	.855	.895	.955	4.65	.926	6.50	1.4
5.93	.860	.890	.966	4.81	.910	7.30	1.5
Average					0.922		1.47

TABLE 6.—*Detailed data for paint c*

Weight, M, of dry solids	Reflectance on black R_0	Reflectance on white $R_{0.80}$	Contrast ratio black/white $C_{0.80}$	Volume, V, of paste	R_∞	SX	S (X in ml/ft.²)
g/ft.²				ml/ft.²			
2.60	0.775	0.855	0.906	2.57	0.880	3.8	1.5
2.87	.785	.850	.923	2.74	.868	4.3	1.6
3.46	.790	.860	.919	3.30	.882	4.2	1.3
3.63	.795	.855	.930	3.46	.872	4.5	1.3
4.27	.820	.860	.953	4.07	.874	5.6	1.4
4.60	.830	.865	.960	4.39	.878	6.2	1.4
4.68	.820	.865	.948	4.47	.881	5.5	1.2
4.88	.835	.870	.960	4.66	.884	6.3	1.4
5.62	.855	.870	.983	5.36	.876	8.9	1.7
5.96	.850	.865	.983	5.69	.870	8.7	1.5
Average					0.876		1.43

TABLE 7.—*Summary for cold-water paints*

Paint	Weight, M, of dry solids for $C_{0.80}$= 0.93	Fraction, K by weight of dry solids in paste	Density, D of paint having K adjusted to 0.5	Volume, V of paste for $C_{0.80}$= 0.93	R_∞	S (X in ml/ft²)	SX for $C_{0.80}$=0.93	Thickness, X for $C_{0.80}$=0.93 found from theory, ml/sq ft (compare with V)	Thickness, X for $C_{0.80}$=0.93 for R_∞ degraded to 0.865 by addition of black pigment, found from theory
	g/ft²		g/ml	ml/ft²					ml/ft²
a1	3.90	0.674	1.51	3.15	0.922	1.47	4.92	3.35	3.05
a2	4.00	.674	1.51	3.25	.916	1.50	4.87	3.25	2.95
b	4.20	.683	1.51	3.30	.901	1.36	4.73	3.50	3.25
c	3.50	.647	1.42	3.35	.876	1.43	4.53	3.15	3.10
d	4.30	.657	1.51	3.65	.928	1.33	4.99	3.75	3.35
e	4.50	.676	1.47	3.80	.904	1.31	4.76	3.65	3.40
f	4.45	.665	1.48	3.80	.865	1.22	4.45	3.65	3.65
g	4.60	.676	1.48	3.80	.912	1.28	4.83	3.75	3.45
h	5.35	.704	1.40	*4.55	.927	1.18	4.98	4.20	3.75
i	5.50	.682	1.47	4.55	.906	1.04	4.78	4.60	4.30

*This value is uncertain because of inconsistencies in data ascribable to unusual difficulty of spreading paint *h* uniformly. This paint requires more water than the others for application.

A plot of contrast ratio, $C_{0.80}$, against weight of dry solids per unit area was also made for each paint, and the weight required to produce a contrast ratio of 0.93 (incomplete hiding) was read from a curve fitted graphically to the plotted points. These values are recorded in table 7, together with the fraction, K, by weight of dry solids in the paste, and the density, D, of paint for which K is adjusted to 0.5. The values of reflectivity, R_∞, and coefficient of scatter, S, recorded in table 7 are the arithmetical means of values derived from all the single coats prepared from the given paint.

(d) DISCUSSION

If the data truly followed the theory, the values of reflectivity, R_∞, and coefficient of scatter, S, should be constant for each paint regardless of the thickness, X, of the coat. Tables 4, 5, and 6 show that there are considerable variations in reflectivity and coefficient of scatter, but since these variations, which are typical of all nine paints studied, are irregular it may be concluded that the data agree with the theory within their uncertainty. The chief source of uncertainty lies in the preparation of a uniform coat of paint so that the central areas measured by the reflectometer will be truly representative of the whole sheet.

As one criterion of the usefulness of white and near-white cold-water paint, the volume, V, of original paste per unit area required to produce incomplete hiding (defined as $C_{0.80}$=0.93) has been proposed; that is, of two paints, the one requiring a smaller volume for incomplete hiding is more economical. However, the hiding power of such paints as these can be increased by adding inexpensive black pigment, and slight additions are permissible. But to prevent excessive darkening of the paint by such additions, it is customary to specify a minimum value of reflectivity, R_∞. On the assumption that all nine paints would meet the latter specification, the paints have been arranged in table 7 in accord with the volume, V, of original paste required per unit area for incomplete hiding. It will be noted that

paints *a* to *c* form a group whose members are nearly equally desirable; and paints *d* to *g* and *h* to *i* form two other similar groups.

This form of specification does not rest upon any theory because reflectivity, R_∞, may be determined directly by measurement of a coat of the paint so thick that it is completely opaque, and volume, V, of the original paste required per unit area for incomplete hiding may be determined as above by graphical curve fitting. It is of interest to show the relation of this specification to the constants, R_∞ and S, of the Kubelka-Munk theory. The volume, V, per unit area required for incomplete hiding may be computed from R_∞ and S by means of the chart given in figure 2. First read SX for $C_{0.80}=0.93$ corresponding to the reflectivity, R_∞, of the paint. These values are given in the eighth column of table 7. Then obtain X for incomplete hiding by dividing SX by S. These values are given in the ninth column of table 7. It will be noted that there is good general agreement between these values and those (fifth column) found by reading a curve fitted graphically. The same three groups having the same members appear in both columns. The cases showing poorest agreement (paints *a*, and *h*) were examined in detail and it was found in each case that the discrepancy is well within the uncertainty of fitting the curve graphically. It is probable that the values obtained by way of the theory are somewhat more reliable because such a method amounts to fitting a curve to the data of a form which is known by extensive study to be closely correct, but in graphical curve fitting the form of the curve has to be derived anew from data obtained for each separate paint.

In addition to providing a fundamental basis for derivation of thickness for incomplete hiding, the Kubelka-Munk theory permits the comparison of paints of different reflectivity as if they had all been degraded by addition of the proper amount of black pigment to the same reflectivity value. Suppose it to be required to find for each paint the volume, V, of original paste needed per unit area to produce incomplete hiding after each had been degraded to a reflectivity of 0.865. The value SX corresponding to $C_{0.80}=0.93$ and to $R_\infty=0.865$ is read from figure 2 and found to be 4.45. The required thickness, X, expressed in milliliters per square foot of original paste, is calculated as $4.45/S$; values are given in the last column of table 7. By comparison of the last two columns, it may be seen that in every case (except, of course, paint *f*, for which $R_\infty=0.865$) the volume of original paste required to produce incomplete hiding has been reduced by the addition of enough nonscattering black pigment to degrade the paint to a reflectivity of 0.865. The effect has been to place paint *f* in the least desirable group. This method of rating paints is thought to be the fairer of the two; it rates them in accord with coefficient of scatter, S.

It is concluded, therefore, that the Kubelka-Munk theory has been shown to apply within the experimental uncertainty to cold-water paints, and also that one of the constants (coefficient of scatter, S) of the theory may be taken as an index of the desirability of white cold-water paint.

3. PAPER

By Deane B. Judd and Merle B. Shaw

Measurements were made to determine whether the fundamental optical properties of paper also follow the Kubelka-Munk equation.

(a) PREPARATION OF SAMPLES

Paper consists mainly of cellulose fibers felted together in a sheet. It is made by depositing, from a dilute water suspension, an even layer of fibers on a screen.

All basic papermaking materials must first be reduced to separate fibers before they can be suspended in water and formed into sheets of paper. Fibers being absorptive, sizing material is added in the preparation of the papermaking stock to make the paper more nearly impervious to ink. Dye also is added if desired. Mineral filling material is sometimes included to fill the voids between the fibers and improve the printing quality of the paper. After the admixture of fiber and nonfibrous papermaking materials (beater furnish) has reached the proper stage of preparation, sufficient water is added to give the desired consistency and the resultant stock is run onto a traveling endless wire cloth. The water drains away as the wire moves forward and the residual thin layer of fibers forms the paper. The sheet is passed over suction boxes, between press rolls and around hollow steam-heated drying cylinders to remove the water. The thickness of paper is determined by the rate of flow of stock (water with fibers in suspension) onto the wire cloth of the paper machine and by the speed of the machine.

The papers used in this study were made in the experimental paper mill of the Bureau by Merle B. Shaw and Martin J. O'Leary. The paper mill contains equipment for the experimental manufacture of practically all types of paper, under conditions which in general simulate those of industrial mills. A complete description of the equipment may be found in previous publications.[15]

The experimental papers were of three types—writing (two grades), book, and newsprint. Each type was of six different basis weights (designated by the letters *A* to *F* in table 8), all made during the same machine run from the same batch of stock, thereby precluding any differences in effects of beating, jordanning, or other processing in the preparation of the stock. Rosin size but no coloring matter was used in the papers. The following describes the papers made.

[15] *Caroá fiber as a papermaking material*, Tech. Pap. BS **21**, 338–341 (1927) T340; *Further experimental production of currency paper in the Bureau of Standards Paper Mill*, BS J. Research **3**, 904–5 (1929) RP121; *Equipment and research work of the Bureau of Standards Paper Mill*, Paper Trade J. **89**, 19, 60–63 (1929).

TABLE 8.—*Detailed results for paper*

Daylight reflectance, R, computed from the brightness ratio, B_{sample}/B_{MgO}, on the assumptions: (*a*) For the Priest-Lange reflectometer, $R_{MgO}=0.970$; (*b*) For the Hunter reflectometer, $R_{MgO}=1.000$

Sample	Ash (bone-dry basis)	X Thickness	X wt (25×40 inches, 500 sheets)	R_0		R_∞		R_g		$C_\infty=R_0/R_\infty$		$C_{0.89}=R_0/R_{0.89}$		TAPPI opacity B&L	R_∞ by chart from R_0 and C_∞		SX		S X=thickness		S X=weight	
				P-L (a)	H (b)	P-L	H	P-L	H	P-L	H	P-L	H		P-L	H	P-L	H	P-L	H	P-L	H
	Percent	*Inch*	*Pounds*																			
RW-A	0.36	0.0028	38	0.691	0.683	0.882	0.890	0.881	0.890	0.783	0.767	0.782	0.767	0.769	0.875	0.890	2.35	2.23	840	800	0.062	0.059
B	.35	.0033	46	.726	.717	.887	.891	.885	.890	.819	.805	.818	.806	.802	.882	.889	2.82	2.66	850	810	.061	.058
C	.32	.0040	53	.754	.752	.887	.891	.883	.891	.850	.844	.852	.844	.847	.880	.891	3.33	3.23	830	810	.063	.061
D	.36	.0045	64	.782	.777	.885	.891	.886	.891	.884	.872	.880	.872	.872	.887	.891	3.95	3.78	880	840	.062	.059
E	.37	.0053	75	.805	.801	.887	.891	.884	.890	.908	.899	.909	.900	.901	.882	.890	4.77	4.52	900	850	.064	.060
F	.38	.0082	111	.849	.842	.889	.890	.889	.890	.955	.946	.954	.946	.950	.888	.890	7.2	6.6	880	810	.065	.059
Avg	0.36					0.886	0.891								0.882	0.890			865	817	0.063	0.059
G				0.885	0.888																	
SW-A	0.38	0.0027	38	0.614	0.606	0.820	0.811	0.848	0.848	0.749	0.747	0.719	0.715	0.712	0.811	0.800	1.72	1.67	640	620	0.045	0.044
B	.38	.0031	46	.656	.646	.818	.809	.845	.841	.802	.799	.772	.768	.768	.814	.801	2.11	2.04	680	660	.046	.044
C	.34	.0037	52	.688	.677	.821	.815	.841	.839	.838	.831	.813	.807	.807	.817	.805	2.50	2.40	680	650	.048	.046
D	.37	.0046	64	.724	.717	.821	.814	.841	.834	.882	.881	.858	.860	.862	.820	.808	3.11	3.06	680	670	.049	.048
E	.35	.0052	76	.746	.740	.822	.817	.837	.833	.908	.906	.888	.888	.887	.820	.813	3.63	3.57	700	690	.048	.047
F	.34	.0081	118	.789	.778	.820	.811	.829	.820	.962	.959	.950	.949	.944	.821	.810	5.50	5.3	680	650	.047	.045
Avg	0.36					.820	0.813								0.817	0.806			677	657	0.047	0.046
G				0.880	0.888																	
B-A	5.80	0.0030	39.1	0.730	0.725	0.831	0.827	0.844	0.845	0.878	0.877	0.862	0.858	0.85	0.825	0.822	3.19	3.12	1060	1040	0.080	0.082
B	5.81	.0035	46.0	.750	.745	.832	.828	.847	.843	.902	.900	.883	.884	.88	.831	.822	3.61	3.58	1030	1020	.078	.078
C	5.76	.0041	53.9	.772	.769	.829	.828	.837	.839	.931	.929	.920	.917	.91	.825	.825	4.48	4.36	1090	1060	.083	.081
D	5.82	.0048	62.5	.785	.785	.831	.829	.839	.838	.945	.947	.933	.937	.93	.830	.827	4.95	5.05	1030	1050	.078	.081
E	5.93	.0059	76.0	.804	.802	.830	.830	.833	.836	.969	.966	.964	.959	.95	.828	.829	6.45	6.2	1090	1050	.085	.082
F	6.22	.0103	129.5	.825	.821	.829	.826	.829	.828	.995	.994	.995	.992	.99	.828	.827	11.3	10.2	1100	990	.087	.079
Avg	5.89					0.830	0.828								0.830	0.825			1063	1043	0.082	0.080
G				0.880	0.888																	
N-A	0.39	0.0040	37	0.603	0.593	0.623	0.611	0.638	0.626	0.968	0.971	0.945	0.947	0.93	0.621	0.609	3.10	3.53	780	760	0.084	0.082
B	.38	.0046	43	.607	.598	.621	.608	.629	.617	.978	.984	.965	.969	.95	.618	.608	3.52	3.56	770	770	.082	.083
C	.38	.0056	53	.616	.605	.624	.610	.627	.614	.987	.992	.982	.985	.98	.621	.609	4.23	4.28	760	760	.080	.081
D	.39	.0064	64	.624	.610	.624	.612	.625	.613	1.000	.997	.998	.995	.99	.625	.612	6.5	5.6	------	900?	.1?	.09?
E	.39	.0075	75	------	.604	------	.605	------	.606	------	.998	------	.997	.99	------	.605	------	6.7	------	900?	------	.09?
F	.39	.0132	122	------	.598	------	.598	------	.598	------	1.000	------	1.000	1.00	------	.598	------	∞	------	∞?	------	0?
Avg	0.39					.623	0.607									0.607			770	747	0.082	0.082
G				0.888	0.888										0.621							

(a) Priest-Lange (P-L) reflectometer.

(b) Hunter (H) reflectometer.

(1) *Writing Papers.*—Writing paper was made from sulphite pulp (designated *SW* in table 8) and from rag half stuff that had been bleached to very good white color (designated *RW* in table 8). 1.5 percent of rosin size was added in each. No filler or dye was used.

(2) *Book Paper.*—The book paper (designated *B* in table 8) contained clay because the beater furnish was paper-machine "broke" (trimmings or torn paper) from previous runs of book papers in which clay had been used. 1.5 to 2 percent of rosin size, based on weight of dry fiber, was added. Data on weight, thickness, and ash for each basis weight of the paper made are given in table 8.

(3) *Newsprint Paper.*—The beater furnish for this run (designated *N* in table 8) was newsprint taken from a roll of commercial newsprint paper. For this run only 0.5 percent of size was used.

It was found impossible to obtain the same finish on the heavy papers, designated *E* and *F* in the table, as was obtained on the lighter-weight papers because of the smallness of the calendar stack. The heavier papers, especially sample *F*, seemed "two-sided." The smoother side was the under- or wire-side; the other side was marked by the couch-roll jacket.

(b) MEASUREMENTS

Measurements of reflectance were made on the Hunter "photox photoelectric" reflectometer and on the Priest-Lange reflectometer. Five samples of each paper were tested, the Hunter reflectometer giving average apparent reflectance over a nearly circular area about 7 cm in diameter, the Priest-Lange reflectometer over a semicircular area of about 1 cm diameter near the center of the sample. The backings used for these measurements were (1) black velvet for which R' was taken equal to zero; (2) an opaque stack of the paper itself for which R' was taken equal to R_∞; and (3) a backing designated as *G* which consisted of an opaque stack of rag writing paper (*RW-F*) for which R' varied from 0.888 to 0.880 because of slight soiling during use. The results of these measurements by the two reflectometers are given in table 8 in parallel columns, the Priest-Lange reflectometer being designated by the letters *P-L*, and the Hunter reflectometer being designated by the letter *H*.

Both of these reflectometers measure apparent reflectance, *A*, relative to magnesium oxide, the Priest-Lange reflectometer illuminating the sample and standard nearly diffusely and viewing them perpendicularly, the Hunter reflectometer illuminating them nearly perpendicularly and viewing them at nearly 45°. The estimated values of reflectance, *R*, given in table 8 for the nearly mat paper samples were found from the Priest-Lange values as $0.97\ A/A_{MgO}$, and from the Hunter values as simply A/A_{MgO}. These estimates are based on the values of A_{MgO} for the respective angular conditions; that is, for the conditions of the Hunter reflectometer $A_{MgO}=1.00$.[16] The estimates are also based on the assumption, known not to be strictly justified, that the paper samples are perfect diffusers, that is, that the light reflected from them is distributed equally in all directions.

Both the Priest-Lange reflectometer readings and those by the Hunter reflectometer are characteristic of observation of the samples

[16] J. S. Preston, *The reflection of magnesium oxide*, Trans. Opt. Soc. **31**, 15 (1929-30).
H. J. McNicholas, *Absolute methods in reflectometry*, BS J. Research **1**, 29 (1928). RP3.
Preparation and Colorimetric Properties of a Magnesium-Oxide Reflectance Standard, NBS Letter Circular LC395.

in daylight by a normal human observer. With the Priest-Lange reflectometer, a visual instrument, this effect was obtained by using a sunlight filter; with the Hunter reflectometer, although the illuminant was a gas-filled lamp, approximately this effect is obtained because the spectral sensitivity of the Photox cell is relatively somewhat higher for the short-wave part of the spectrum than the spectral luminosity curve for the average eye.

There are also shown in table 8 values of TAPPI opacity for these papers obtained from a photoelectric opacimeter designed by M. N. Davis.[17] In this opacimeter the sample is illuminated nearly perpendicularly by incandescent-lamp light and is viewed diffusely by means of an integrating cube and photronic cell.

(c) REDUCTION OF DATA

Entries in the column headed, $C_\infty = R_0/R_\infty$, of table 8 were obtained by simple division of values of R_0 by R_∞. This ratio for paper has been used considerably under the name of printing opacity.

Entries in the column headed $C_{0.89} = R_0/R_{0.89}$ were computed from R_0 and R_G. This computation would have been simple division provided sample G had turned out to have a reflectance of exactly 0.89. Since, however, in some cases the reflectance of sample G departed by as much as 0.01 from 0.89, corrections read from figure 5 were applied. As an example of the way to apply these corrections take sulphite writing paper of the least thickness ($SW-A$). The reflectance over a black backing, R_0, is estimated from the results by the Priest-Lange reflectometer as 0.614 (see table 8); that over backing G, as 0.848. The ratio, R_0/R_G, is 0.724, and since backing G had a reflectance during this reading of 0.880, this result could be written: $C_{0.88}=0.724$. To find $C_{0.89}$ for this sample refer to figure 5 (upper plot). For $C_{0.90}$ in the neighborhood of 0.72 and for R_0 about 0.61, the value of the correction, $C_{0.80}-C_{0.90}$, for a deviation of R' of 0.10 is seen to be about 0.047. Since this case yields a deviation in R' of only 0.01, the correction is taken as one-tenth the value read from figure 5, that is, the correction to be applied is 0.005. The value of $C_{0.89}$ is, therefore, $0.724-0.005=0.719$.

Values of R_∞ and SX were read from R_0 and $C_{0.89}$ by means of figure 1. From the values of SX, S was computed both for X taken as basis weight in pounds per 500 sheets of 25 by 40 inches and X taken as thickness in inches.

(d) DISCUSSION

It may be noted that for the writing paper and the newsprint paper estimates of reflectance from readings of the Priest-Lange reflectometer tend to be higher by about 1 percent than those from readings of the Hunter reflectometer. For the book paper the difference is in the same sense but considerably less. The data from the two instruments have been reduced separately so that the amount of the differences may be traced through to the end. These differences are evidently related to angular distribution of the reflected light; and, in fact, for some other materials the differences are in the opposite direction.

Values of $C_{0.89}$, since they refer to daylight as illuminant, are not quite comparable with those of TAPPI opacity obtained by the Davis

[17] See footnote 11, p. 295.

(B & L) opacimeter, which refer to incandescent-lamp light. The yellower light from the incandescent lamp is expected to penetrate paper more readily because both absorption and scattering coefficients of these papers are lower for long-wave light, and this greater penetration results in values of TAPPI opacity somewhat lower than those of $C_{0.89}$, obtained from the Priest-Lange reflectometer. The angular conditions of illuminating and viewing for these two instruments are nearly reciprocal; hence, they would be expected to yield comparable

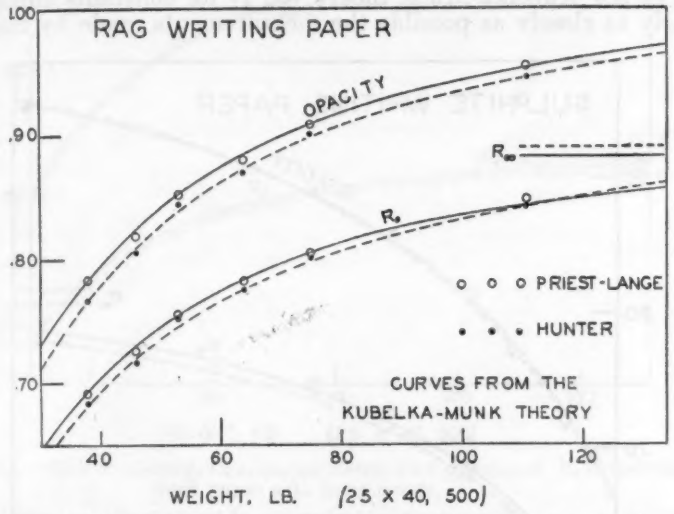

FIGURE 10.—*Rise in opacity, $C_{0.89}$ (upper curve) and reflectance, R_0, (lower curve) of rag writing paper with basis weight.*

The plotted points are estimates based on measured values of apparent reflectance A_8; the curves are from the Kubelka-Munk theory.

results were it not for the difference in spectral energy distribution of illuminant. The Hunter reflectometer on the other hand uses both unidirectional illumination and unidirectional viewing; so it would not be expected to yield results exactly comparable to the other two instruments, which use either diffuse illumination or diffuse viewing. It is of interest, however, to note that $C_{0.89}$ by the Hunter reflectometer is in good agreement with TAPPI opacity. This suggests that for these papers the disparity in spectral distribution of illuminant and receptor sensitivity has by a coincidence been closely compensated for by the difference in angular distribution.

The agreement between the observed reflectivities, R_∞, and those obtained from the chart is good, the differences in all but two or three cases being less than the uncertainty of the experimental results. There is a significant tendency, however, exhibited in most of the results, for reflectivity estimated by the chart (fig. 1) based on the Kubelka-Munk theory to be lower than that directly measured, the thinner papers showing the greater discrepancy. It is concluded, therefore, that the Kubelka-Munk theory does not apply strictly to papers measured in the usual way with these reflectometers. The causes for the slight discrepancies are not known definitely.

The coefficients of scatter show a similar tendency to be slightly lower for the lower thicknesses of paper, although this tendency is of

doubtful significance for the book papers. A possible explanation of the tendency of both reflectivity and coefficient of scatter to be low for thin samples of the nonweighted papers is that the water in draining out of the thin samples carried away disproportionately large numbers of fine white particles compared to thicker samples.

The degree of agreement between the measurements and the Kubelka-Munk theory is also shown in figures 10, 11, and 12. The plotted points represent the results of measurement; the solid curves represent the Kubelka-Munk theory (eq 1) for constants adjusted to fit nearly as closely as possible the measurements made by means of

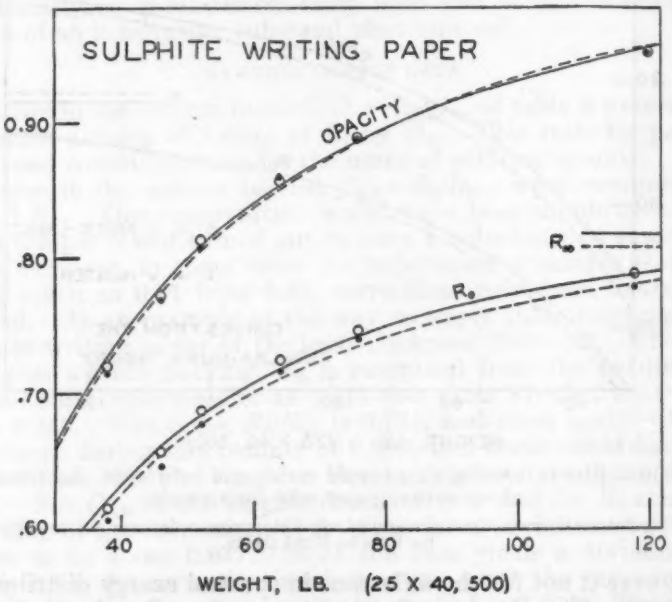

FIGURE 11.—*Rise in opacity, $C_{0.89}$ (upper curve) and reflectance, R_0 (lower curve) of sulphite writing paper with basis weight.*

The plotted points are estimates based on measured values of apparent reflectance, A_0; the curves are from the Kubelka-Munk theory.

the Priest-Lange reflectometer; the dotted curves similarly represent the theory fitted to the measurements made by the Hunter reflectometer. These graphs show the measured rise in reflectance over black backing, R_0, and the measured rise in opacity compared to the respective theoretical variations. The small but significant deviations from the theory are evident as is also the rather closer fit to theory obtained with the rag writing and book papers. Results for the newsprint papers are omitted because of the restricted range in opacity obtained.

It is concluded that, except for deviations of less than 1 percent, the Kubelka-Munk theory applies to paper; the two constants of the theory, reflectivity, R_∞, and coefficient of scatter, S, yield a useful description of the material of which paper is made. This holds both for X, as thickness and for X as basis weight. By means of a description in these terms the optical properties of the papers made from the four types of furnishes studied may be predicted within 1 percent

over the whole practical range of basis weights. The constants may also be correlated with the appearance and composition of the paper.

Table 9 gives a summary of the average characteristics determined from the Hunter reflectometer for the four types of paper studied. Average values of ash are also included.

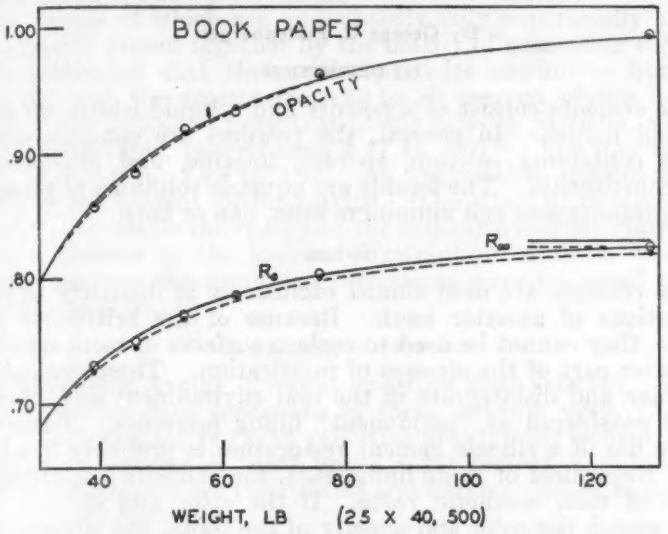

FIGURE 12.—*Rise in opacity, $C_{0.89}$ (upper curve) and reflectance, R_0 (lower curve) of book paper with basis weight.*

The plotted points are estimates based on measured values of apparent reflectance, A_0; the curves are from the Kubelka-Munk theory.

TABLE 9.—*Summary for paper*

Type of paper	Reflectivity, R_∞	Coefficient of scatter, S		Ash
		Per inch	Per pound	
Rag writing	0.89	820	0.059	0.36
Sulphite writing	.81	660	.046	.36
Book	.83	1,040	.080	5.89
Newsprint	.61	750	.080	0.39

Reflectivity is seen to be highest for the rag-writing paper and lowest for the newsprint paper; it correlates with usefulness of the paper to form a background for legible dark letters and it also correlates with the cost of the paper.[18] Coefficient of scatter expressed per unit basis weight is lowest for sulphite writing paper and highest for the book and the newsprint. The increased coefficient of scatter for the book paper over the rag writing paper may be ascribed to the presence of clay filler (note high ash); that for newsprint paper may be ascribed to the presence of groundwood. Coefficient of scatter expressed per unit thickness is also lowest for the sulphite writing paper, but that for the newsprint paper is in this case considerably

[18] A better index of cost than daylight reflectivity is reflectivity for blue light (often called "brightness") See L. C. Lewis, *Definition of brightness*, Paper Trade J. **101**, no. 6, TS64 (August 8, 1935); *Recent progress on color problems in the paper industry*, Paper Trade J. **103**, no. 22, TS323 (November 26, 1936).

lower than that for the book paper. This corresponds to the greater bulk of the newsprint paper.

This general applicability of the Kubelka-Munk theory to paper is in agreement with the less detailed reports by Steele [19] and Lewis.[20]

4. DENTAL SILICATE CEMENTS [21]

By George C. Paffenbarger

(a) DEFINITION

These cements consist of a powder and a liquid which, on mixing, react and harden. In general, the powders are complex aluminosilicates containing calcium, sodium, fluorine, and phosphorus as major constituents. The liquids are aqueous solutions of phosphoric acid containing zinc and aluminum salts, one or both.

(b) USE

These cements are used almost exclusively in dentistry to replace lost portions of anterior teeth. Because of the brittleness of the cements, they cannot be used to replace surfaces of teeth which bear the greater part of the stresses of mastication. These cements tend to dissolve and disintegrate in the oral environment and, therefore, are not considered as "permanent" filling materials. The average effective life of a silicate cement restoration is probably less than 3 years. Regardless of these limitations, the cements are widely used because of their aesthetic value. If the color and opacity of the cement match the color and opacity of the tooth, the silicate cement restoration blends with the tooth structure and is difficult to detect. Thus, the opacity is a very important element in the evaluation of the cement.

(c) PREPARATION OF SPECIMENS

The cements were mixed on a glass slab with an agate spatula by the common dental method. Disks of the cement were formed by pressing the plastic cement between two flat glass plates which were separated by gage blocks of the desired thickness. After the initial hardening had occurred the specimen was immersed in distilled water and was kept under water at all times to prevent deterioration.

(d) METHOD OF MEASUREMENT

Measurements of reflectance of the cement specimens covered with water were made on a Priest-Lange reflectometer. Because the specimen could be brought into focus in the photometric field of this instrument, thus permitting comparisons of different parts of the specimen, it was possible to use specimens of a minimum area. Furthermore, the reflectance of small sections of human enamel and dentin could be determined with this instrument. Until the opacity of tooth tissue could be determined, it was difficult to establish rational opacity requirements for the silicate cements.

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[19] F. A. Steele, *The optical characteristics of paper. I. The mathematical relationships between basis weight, reflectance, contrast ratio, and other optical properties*, Paper Trade J. **100**, no. 12, 37 (March 21, 1935).

[20] L. C. Lewis, *Recent progress on color problems in the paper industry*, Paper Trade J. **103**, no. 22, TS323 (November 26, 1936).

[21] Geo. C. Paffenbarger, and Irl C. Schoonover, *Physical properties of dental silicate cements (abstract)*, J. Dental Research **15**, 322 (September 1936). For a detailed report, see Paffenbarger, Geo. C., Schoonover, Irl C., and Souder, Wilmer, *Silicate cements, physical and chemical properties, and a specification.* To be published in volume 24 (1937) of the J. American Dental Association.

Because the reflectance of a substance is in general a function of the wave length of the incident light and because, in ordinary conditions of use of dental cements, daylight is the incident light, a "daylight" filter was employed. The reflectances and contrast ratios given in this section of the report are, therefore, for artificial noon sunlight.

A hardened specimen of cement consists of numerous particles of powder (many of which are undoubtedly only superficially attacked by the liquid) bound together by the matrix of cementing substance. It was estimated that the powder particles amount to from 70 to 80 percent and the matrix from 20 to 30 percent of the hardened cement. The indices of refraction of the powder particles, which are almost all isotropic, ranged from 1.47 to 1.60.[22] The indices of the matrix varied from 1.45 to 1.48. An appreciable amount of air is trapped in the cement during mixing. The effect of multiple reflections of the air-water interface and the cement-water interface caused by the difference in the indices of refraction of these media was neglected because the computed corrections were too small to affect the results significantly.

(c) DISCUSSION OF DATA

Three cements having different opacities were selected. The $C_{.70}$ values of 1 mm-thick specimens of these cements were: Cement F (white), 1.00; cement D (light yellowish gray), 0.43; cement D (light yellow), 0.41; cement K (dark gray), 0.32; cement K (white), 0.24. White and dark gray are the lightest and darkest shades, respectively, which are in common use.

The R_∞ and S values obtained from figure 3 for these cements were not as concordant as for the other materials tested. These variations are too great to be ascribed to photometric uncertainty, and the data on cement K (white) suggest that variations among R_∞ and S values may be caused by inhomogeneities among specimens. In preparing the larger specimens, mixes 100 times larger than those used in ordinary dental operations, were necessary. This made it difficult to disperse the powder particles and the trapped air bubbles evenly before the cement began to set.

The constants R_∞ and S can be correlated with the composition of the cements. For example, cement F, the powder of which contains over 50 percent of zinc oxide, has the highest coefficient of scatter, S. Cements D and K are similar in chemical composition but their respective powder particles have a different physical structure. Petrographic analysis revealed that the powder particles of cement D were cloudy, while those of cement K were clear. This distinction correlates with the higher S value of cement D. Note also that the reflectivities, R_∞, of cements K, white and gray, are high and low, respectively, while the S values are approximately the same. A possible interpretation is that the dark-gray cement was produced by adding a nonscattering black pigment to the white cement.

The data (table 10) indicate that the formula of Kubelka and Munk is applicable to dental silicate cements within the rather large uncertainty involved in the preparation of specimens.

[22] Petrographic examinations were made by H. Insley.

TABLE 10.—*Reflectance data for silicate cements*

Cement [1]		X	R_0	$C_{0.76}$	R_∞	SX	S
Code letter	Color						
		mm					
F	White	0.37	0.649	0.874	0.76	2.25	0.61
F	do	.58	.713	.952	.76	3.69	.64
F	do	.82	.722	.980	.74	5.00	.61
F [2]	do	.37	.653	.870	.77	2.23	.60
F [2]	do	.58	.720	.950	.77	3.70	.64
F [2]	do	.82	.737	1.000	.74	[3]	------
D	Light yellow	.52	.145	.218	.50	.178	.34
D	do	.85	.224	.356	.50	.317	.37
D	do	1.06	.262	.434	.49	.405	.38
D	Light yellowish-gray	.50	.141	.234	.40	.184	.37
D	do	.82	.207	.370	.40	.304	.37
D	do	1.14	.274	.502	.43	.468	.41
K	White	2.10	.291	.440	.60	.442	.21
K	do	3.03	.326	.575	.48	.610	.20
K	do	4.75	.481	.786	.58	1.2	.26
K [4]	do	2.10	.261	.395	.59	.375	.18
K [4]	do	3.03	.309	.543	.47	.545	.18
K [4]	do	4.75	.431	.708	.56	.970	.20
K [5]	do	2.02	.265	.390	.63	.380	.19
K [5]	do	3.26	.368	.586	.57	.683	.21
K [5]	do	4.96	.486	.784	.59	1.27	.26
K [6]	do	2.00	.262	.390	.62	.370	.19
K [6]	do	3.28	.437	.660	.63	.900	.27
K	Dark gray	1.95	.137	.639	.16	.351	.18
K	do	3.04	.152	.880	.16	.566	.19
K	do	4.72	.153	.940	.16	.700	.15

[1] Specimens were 1-week old, except where noted.
[2] Same as F except specimens were 18 days old.
[3] Could not read on plot (fig. 3).
[4] Same as K (white), except specimens were 18 days old.
[5] [6] Additional 1-week-old specimens of K (white).

V. SUMMARY

It is concluded that the simple Kubelka-Munk theory applies to reflectance measurements of vitreous enamel, cold-water paint, paper, and dental silicate cements, made on the usual reflectometers in the usual ways. Either no regular deviations of theory from actual measurement are found, or the deviations found are of about the order of magnitude of the experimental uncertainty. It will be noted that the agreement between theory and experiment is as good for materials whose medium differs from air (vitreous enamel and dental silicate cement) as it is for materials having air as the medium (paper and cold-water paint). It would seem, therefore, that corrections for light reflected from the inner side of the air-medium face are negligible. Description of these materials by means of the two constants of the theory, reflectivity and coefficient of scatter, is, therefore, of practical validity and use. The most valuable use of the methods described herein is to differentiate in a fundamental way between various members of the same group of materials. Such differentiations are illustrated in tables 1 and 2 (vitreous enamels); 4, 5, 6, and 7 (cold-water paints); 8 and 9 (papers); and 10 (dental silicate cements). These methods also permit comparisons to be made between different classes of materials. Such comparisons are

shown in table 11 in which the coefficient of scatter refers to thickness expressed in microns for all materials. It will be noted that materials whose scattering elements are distributed in air (cold-water paint, paper) have higher coefficients of scatter. Note also that vitreous enamels have a much higher coefficient of scatter than dental silicate cements; this corresponds to the different purposes of the two materials, the one to hide the ground coat with as thin a layer as possible, the other to match fairly translucent tooth enamel.

TABLE 11.—*Summary*

Material	Reflectivity, R_∞	Coefficient of scatter, S (thickness in microns)
VITREOUS ENAMEL		
1	0.89	0.0100
2	.90	.0090
3	.89	.0064
4	.82	.0056
COLD-WATER PAINT		
a	0.92	0.084
b	.90	.075
c	.88	.090
d	.93	.079
e	.90	.075
f	.86	.072
g	.91	.073
h	.93	.065
i	.91	.059
PAPER		
Rag writing	0.89	0.032
Sulphite writing	.81	.026
Book	.83	.041
Newsprint	.61	.030
DENTAL SILICATE CEMENT		
F (white)	0.76	0.0006
D (light yellow)	.50	.0004
D (light yellowish gray)	.40	.0004
K (white)	.59	.0002
K (dark gray)	.16	.0002

The methods and graphical aids presented herein serve not only for the derivation of the fundamental constants of a light-scattering material according to the Kubelka-Munk theory but also for the reverse derivation, that of the reflectance and opacity of any thickness of the material of known constants. They also indicate the effect on reflectance and opacity produced by adding nonscattering dye or pigment. By means of these methods and graphical aids it has been found convenient to apply the Kubelka-Munk theory, and this theory has been useful in research as well as in the specification of light-scattering materials.

WASHINGTON, July 2, 1937.

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PARAFFIN HYDROCARBONS ISOLATED FROM CRUDE SYNTHETIC ISOOCTANE (2,2,4-TRIMETHYLPENTANE)

By Donald B. Brooks, Robetta B. Cleaton, and Frank R. Carter

ABSTRACT

In connection with a study of the impurities present in the isooctane (2,2,4-trimethylpentane) certified for use as a primary standard reference fuel for the knock testing of motor fuels, a number of isoparaffin hydrocarbons have been obtained in a state of relatively high purity. The physical properties of these preparations which have been accurately measured include in most cases the freezing point, ASTM octane number, boiling point, refractive index, and density, the coefficients of variation of the last two with temperature, and the coefficient of variation of boiling point with pressure.

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I. ORIGIN AND SCOPE OF INVESTIGATION

Normal heptane and the isooctane (2,2,4-trimethylpentane) are the compounds which have been adopted internationally as the primary standard reference fuels for the knock rating of automotive-engine fuels. In the latter part of 1934, the Cooperative Fuel Research Steering Committee, through its Subcommittee on Methods of Measuring Detonation,[1] requested the National Bureau of Standards to make an investigation of the impurities in these primary standards, with a view to developing specifications for purity.

As these materials are used for knock rating, it was necessary to determine not only the amount of each impurity present, but also its knock rating, as the total contamination which can be tolerated depends on the antiknock values of the constituents. Relatively large amounts of material had to be obtained in a state of reasonably high purity, as a knock rating requires a sample of about 200 ml. Smaller amounts of material of higher purity were obtained where possible and several physical properties of the purest materials were measured. In several instances preparations were obtained which appeared to be of higher purity than those heretofore described.

[1] Now the CFR Motor Fuels Committee.

II. SOURCE MATERIALS

As certified isooctane has averaged about 99 percent pure, it is obvious that a very large amount of material would have to be processed in order to obtain the required amount of each impurity. However, the final purification of crude isooctane is by distillation, and the Röhm & Haas Co., manufacturers of isooctane, had on hand a quantity of forerun and still residue from this operation. They kindly offered to supply the quantity of each material required for this work. A total

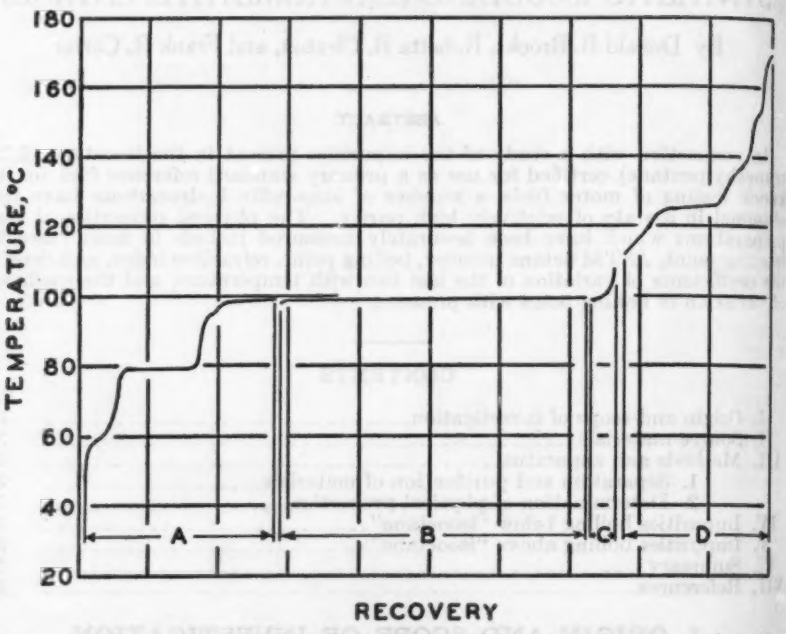

FIGURE 1.—*Composite of fractional distillation of isooctane, forerun, and residue.*

Portion A is the forerun from the purification of crude isooctane, *B* is a distillation of a sample of certified "isooctane", *C* is the distillation, in a small still of the residue from *B*, and *D* is the still residue from the purification of crude isooctane.

of 6 gallons of forerun and a like amount of still residue were obtained from them. This represents the material rejected from over 300 gallons of crude isooctane.

A general picture of the materials involved is given in figure 1. In this figure the portion *A* represents data obtained in the first fractional distillation of the Röhm & Haas forerun. Portion *B* was obtained from a fractional distillation of a sample of batch 12 certified "isooctane", and *C* represents the distillation, in a small still, of the residue from *B*. Portion *D* shows data obtained in the first fractional distillation of the Röhm & Haas residue. The chart is arranged to show the relations between the boiling ranges of the three materials. The scales of recovery for the forerun and the still residue are magnified relative to that for the certified isooctane, the forerun being actually 1.25 percent, and the still residue 2.16 percent, of the crude isooctane. The principal impurities cause the flat portions at 79 and 125° C.

III. METHODS AND APPARATUS

1. SEPARATION AND PURIFICATION OF MATERIALS

The forerun material was systematically distilled in 2.5-liter lots through fractionating columns packed with locket chain and having an efficiency of about 60 theoretical plates. The distillate was cut into portions boiling as follows: below 78° C, 78 to 81° C, 81 to 99.1° C, 99.2° C, and over 99.2° C. Similar fractions from successive lots were combined. When the entire supply of forerun had been so processed, each portion was again fractionated. Redistillation of each portion resulted in rejecting a certain amount of material to the next lower- and to the next higher-boiling portion, so that some further processing was required. In some cases, four successive fractionations were employed.

The still-residue material was first fractionated in a 30-plate bubble-cap column, and cut at 10° intervals up to 140° C, and at 20° intervals beyond 140° C. These cuts were then redistilled in locket-chain columns. For material normally boiling below 130° C the distillation was carried out at atmospheric pressure, while for that normally boiling above 130° C it was carried out at 215 mm Hg pressure.

In the further treatment of fractions, distillation was used when the quantity available was over 600 ml, and fractional crystallization by equilibrium melting [1],[2] or crystallization from methane when the quantity was less. Crystallization from methane by the method developed by R. T. Leslie [2] was found to be decidedly superior to fractional crystallization without solvent, although, in some cases, it was inferior to distillation where sufficient material was available to make the latter possible.

2. DETERMINATION OF PHYSICAL PROPERTIES

Freezing points of samples were determined by means of apparatus described elsewhere [3]. A platinum resistance thermometer, frequently calibrated, was used for temperature measurement. Reproducibility of freezing points was ordinarily about 0.03° C for materials of medium purity.

Boiling points of samples of low purity were measured in a Cottrell boiling-point apparatus, using mercury-in-glass thermometers which were calibrated frequently. Samples of higher purity were distilled through a 10-inch jacketed column [4], the jacket being heated electrically to a temperature such that slight condensation occurred in the column. This temperature was from 3 to 6° C below the boiling point of the sample. A platinum-resistance thermometer inserted in the column was used for the boiling-point measurement. The barometer used for air-pressure measurement was a Fuess Standard, graduated to 0.01 mm. Reproducibility of results, when corrected to 760 mm Hg, was about 0.01° C. All tabulated data given herein have been corrected to 760 mm Hg pressure.

Refractive indices of samples were measured on an Abbe refractometer (Valentine) graduated to 0.0001. This instrument was calibrated whenever tests were made, by measuring the index for distilled water, and for a sample of octane the index of which had been determined on a spectrometer. Results given in the tables herein are at 20 and 25° C for the *D* line of sodium.

[1] Figures in brackets refer to the references listed at the end of this paper.

Densities of less pure samples were measured by weighing a known volume on an analytical balance. Samples of high purity were measured by a pycnometer. All densities given in the tables herein are at 20° C, and are expressed as grams per milliliter.

IV. IMPURITIES BOILING BELOW "ISOOCTANE"

The forerun received from Röhm & Haas was found to consist of approximately 2 percent of pentanes, 5 percent of hexanes, 20 percent of heptanes, 72 percent of 2,2,4-trimethylpentane, and 0.5 percent of the higher-boiling compounds.

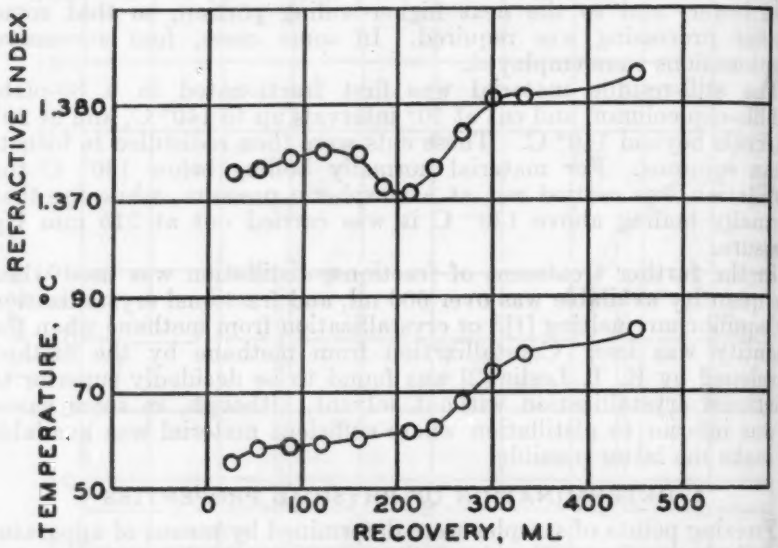

FIGURE 2.—*Data obtained in fractional distillation of material originally fractionated below 78° C.*

The boiling point of the first fraction of the distillation of the forerun, which varied from 48 to 55° C for different lots, suggests the presence of 2,2-dimethylbutane. The amount of this material recovered was not sufficient to make possible its positive identification.

A second fractionation of 1,100 ml of material fractionally distilling originally below 78° C yielded 450 ml of distillate. Data obtained on the fractions are shown in figure 2. Two hexanes were obtained from different portions of this material by fractional crystallization. The properties of these hexanes, designated as materials 1.12C and 1.13C, are given in table 1. The properties found in the literature for hexanes boiling in this range are also given in table 1 for comparison.

TABLE 1.—*Properties of hexanes*

Material	Boiling point, 760 mm Hg	Refractive index		Freezing point	ASTM octane number
		n_D^{20}	n_D^{25}		
	°C			°C	
1.12C	59.1	1.3798	1.3774	−145.5	83.4
1.13C	61.8	1.3729	1.3706	−153.2	83.6
2,3-Me_2Butane [6,14]	58.02	1.3783		−132.7	
2-MePentane [6,14]	60.27	1.372		−153.71	

A third successive fractional distillation of the portions of the forerun boiling between 78 and 81° C was made. The change of refractive index, boiling point, and freezing point throughout this distillation suggested the presence of a slightly higher-boiling compound in addition to the 2,2-dimethylpentane responsible for the flat at 79.2° C on the boiling-point curve. A fourth fractional distillation was made in a smaller still, charging the latter fractions and the still

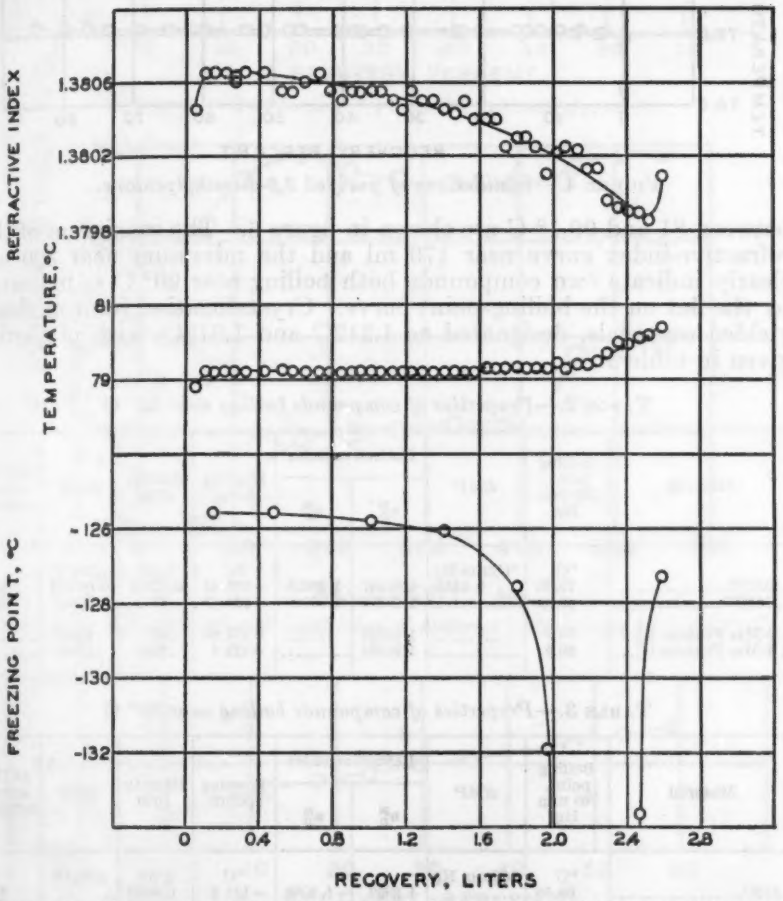

FIGURE 3.—*Composite of fractional distillation of 2,2- and 2,4-dimethylpentane.*

residue of the third distillation. The data obtained in this and the previous distillation have been combined and plotted in figure 3 and suggest the presence of 2,4-dimethylpentane. Two fractional crystallizations of the purer fractions of the less volatile material yielded a compound with a freezing point of 1.5° C below that found by Edgar and Calingaert [5] for synthetic 2,4-dimethylpentane. The properties of this material, designated as 1.2354CC, and of the purest 2,2-dimethylpentane, 1.233CC are given in table 2. The properties given by Edgar, Calingaert, and Marker for these compounds are also listed in table 2 for comparison. Distillation curves for the

purest samples of the two materials are shown in figures 4 and 5. Observations at two different values of atmospheric pressure have been corrected to 760 mm Hg pressure and are indicated by the two symbols in figure 4.

Data from the third fractionation of material originally boiling

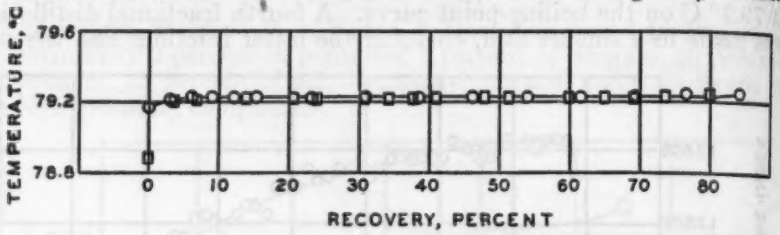

FIGURE 4.—*Distillations of purified 2,2-dimethylpentane.*

between 81 and 99.1° C are shown in figure 6. The maximum of the refractive-index curve near 170 ml and the minimum near 390 ml, clearly indicate two compounds both boiling near 90° C as indicated by the flat on the boiling-point curve. Crystallization from methane yielded materials, designated as 1.312C and 1.313C, with properties given in table 3.

TABLE 2.—*Properties of compounds boiling near 80° C*

Material	Boiling point, 760 mm Hg	dt/dP	Refractive index		Freezing point	Density $D/20$	dD/dt	ASTM octane number
			n_D^{20}	n_D^{25}				
	°C	°C/mm Hg			°C	g/ml	g/ml/°C	
1.233CC	79.23	0.0445	1.38247	1.38023	−125.43	0.67513	0.000804	92.5
1.234CC	80.41		1.38175	1.37949	−124.82	.6731	.00082	90.1
2, 2-Me$_2$ Pentane [5]	78.9		1.38233		−125.60	.6737	.000855	
2, 4-Me$_2$ Pentane [5]	80.8		1.38233		−123.4	.6745	.000856	

TABLE 3.—*Properties of compounds boiling near 90° C*

Material	Boiling point, 760 mm Hg	dt/dP	Refractive index		Freezing point	Density $D/20$	dD/dt	ASTM octane number
			n_D^{20}	n_D^{25}				
	°C	°C/mm Hg			°C	g/ml	g/ml/°C	
1.312C	89.50		1.3892	1.3868	−133.3	0.6880		84.5
1.313C	90.23	0.0437	1.3882	1.3856	−134.3	.6857	0.00092	84.2
2, 3-Me$_2$ Pentane [5]	89.7		1.39201			.6952	.000848	
2-MeHexane [5]	90.0		1.38509		−119.10	.6789	.000855	

The properties found in the literature for hydrocarbons boiling near 90° C are given for comparison. Distillations of the purest samples of these materials are shown in figures 7 and 8.

In addition to the compounds described above, the Röhm & Haas forerun contained about 0.5 percent of material distilling above 99.2° C. A subsequent distillation of this material, the data of which are plotted in figure 9, indicates the presence in the forerun, and consequently in the product to a greater extent, of materials boiling as high as 136° C.

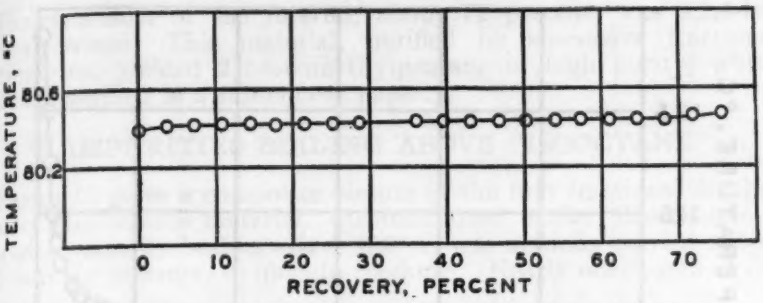

FIGURE 5.—*Distillation of purified 2,4-dimethylpentane.*

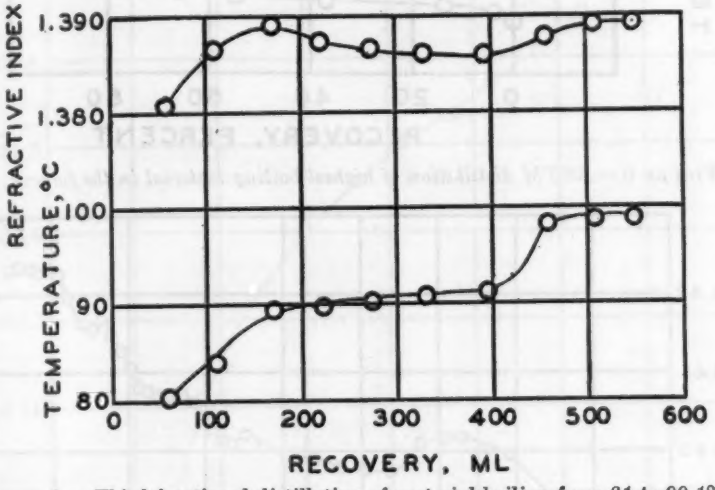

FIGURE 6.—*Third fractional distillation of material boiling from 81 to 99.1° C.*

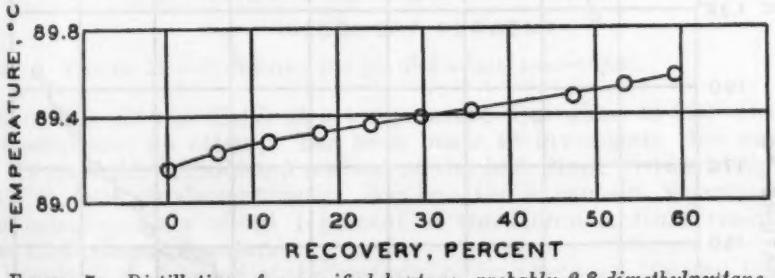

FIGURE 7.—*Distillation of a purified heptane, probably 2,3-dimethylpentane.*

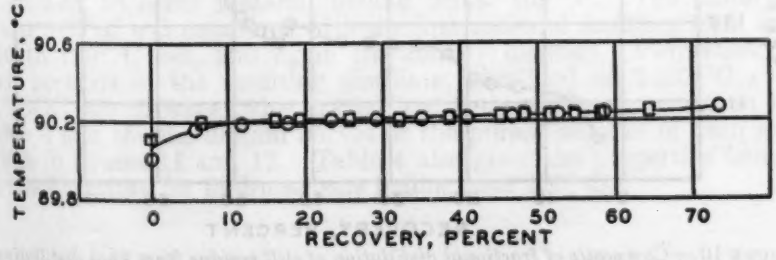

FIGURE 8.—*Distillations of a purified heptane, probably 2-methylhexane.*

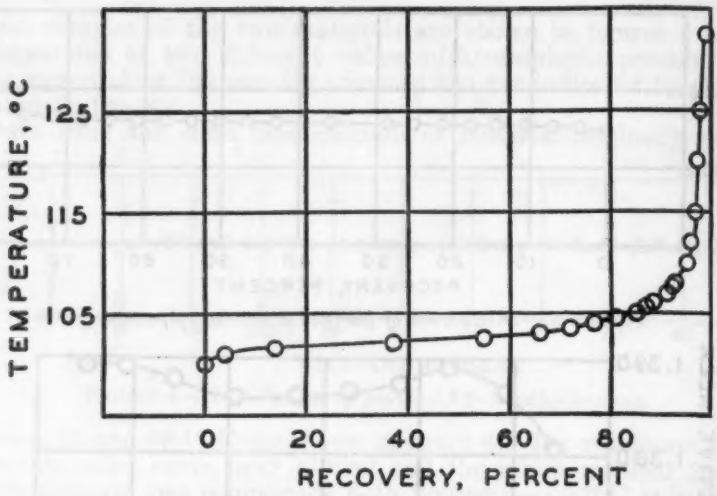

FIGURE 9.—*ASTM distillation of highest-boiling material in the forerun.*

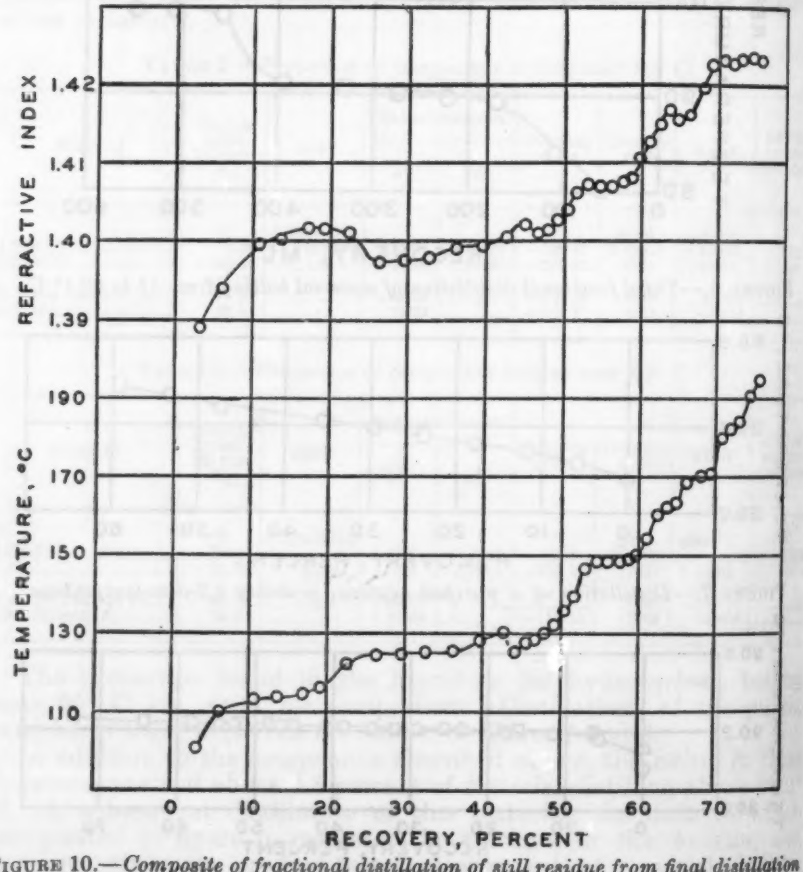

FIGURE 10.—*Composite of fractional distillation of still residue from final distillation of crude isooctane.*

The remainder of the forerun, about 72 percent, was 2,2,4-trimethylpentane. This material, purified by successive fractional distillations, yielded 2,2,4-trimethylpentane of high purity, which will be described in a subsequent paper.

V. IMPURITIES BOILING ABOVE "ISOOCTANE"

Figure 10 gives a composite picture of the first fractional distillation of still-residue material. As mentioned earlier, distillation of material normally boiling above 130° C was actually carried out at 215 mm Hg pressure, to obviate cracking. Nearly one-fourth of the

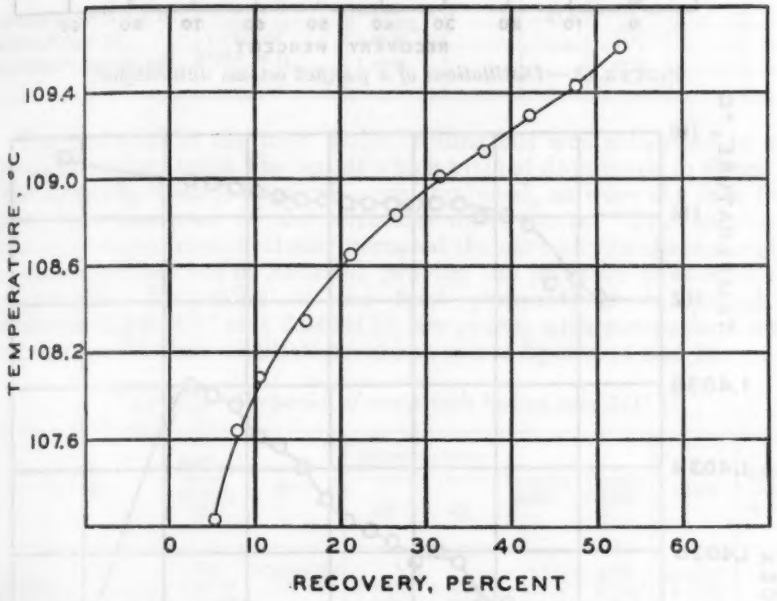

FIGURE 11.—*Distillation of a purified octane, unidentified.*

still residue did not distill at a temperature equivalent to 200° C at 1 atmosphere; no attempt has been made to investigate this part of the material. About 0.5 percent of the base stock distilled below 99.2° C; from its characteristics, it is believed to contain "isooctane" and octenes. Only about 1 percent of the Röhm & Haas residue was 2,2,4-trimethylpentane.

Fractional distillation of the material boiling between 100 and 110° C showed no other material boiling below 109° C. The material above 109° C was combined with the first material distilling from the 110 to 120° C cut, and again fractionally distilled. Properties of two portions of the resulting distillate, identified as 2.322CC and 2.323CC, which were twice crystallized from methane, are given in table 4 and the distillation curves of the purest samples of each are given in figures 11 and 12. Table 4 also gives the properties found in the literature for hydrocarbons boiling near 110° C.

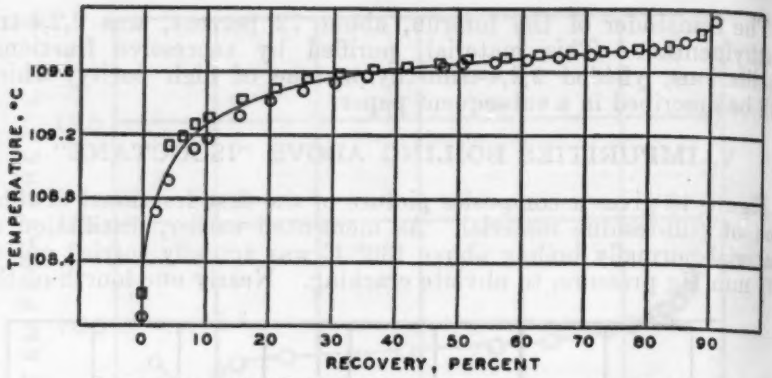

FIGURE 12.—*Distillations of a purified octane, unidentified.*

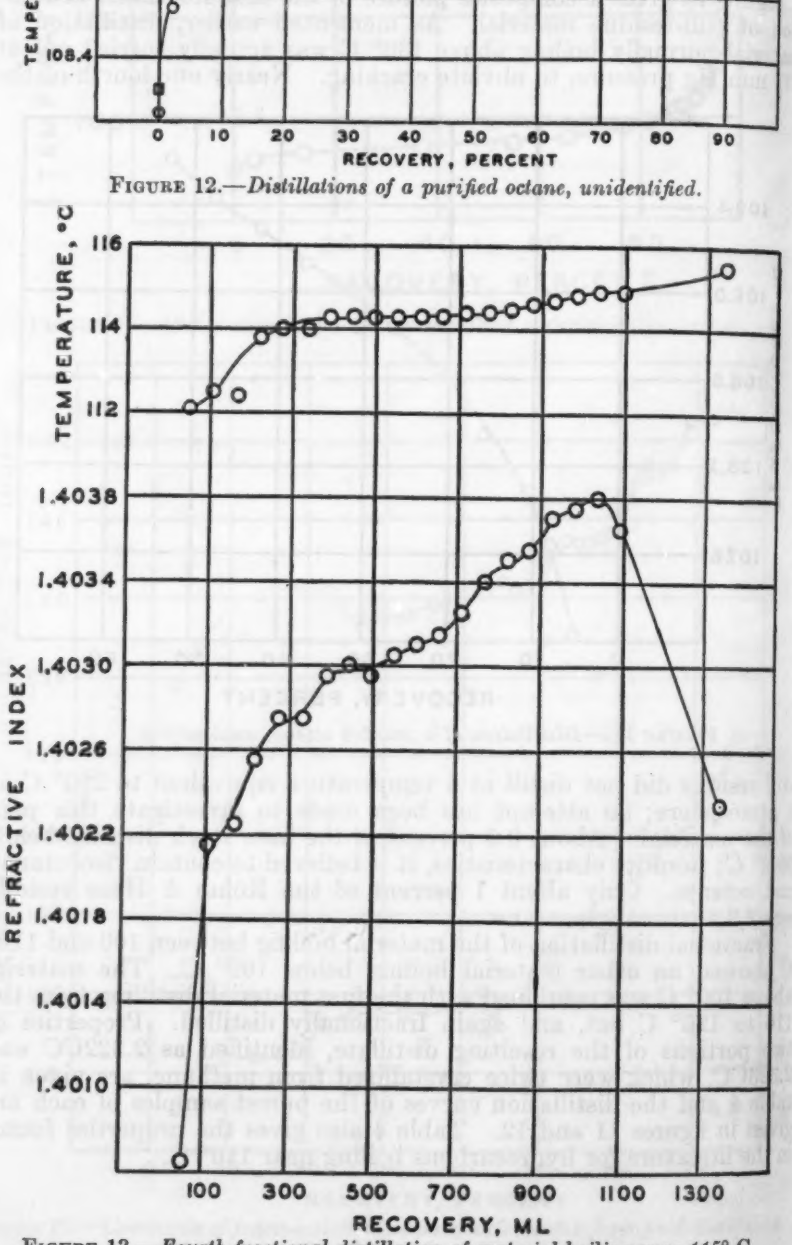

FIGURE 13.—*Fourth fractional distillation of material boiling near 115° C.*

TABLE 4.—*Properties of compounds boiling near 110° C*

Material	Boiling point, 760 mm Hg	dt/dP	Refractive index		Freezing point	Density D/20	dD/dt	ASTM octane number
			n_D^{20}	n_D^{25}				
	°C	°C/mm Hg			°C	g/ml	g/ml/°C	
2,3,3-Me$_3$Pentane [10]	109.5		1.39926	1.39710	−125.0	0.7056		94.8
2,3,3-Me$_3$Pentane [10]	109.65	0.0493	1.40069	1.39852	−122.4	.7108	0.00082	88.3
2,2-Me$_2$Hexane [7]	106 to 107		1.3931			.6967		
2,4-Me$_2$Hexane [6, 8]	108.4 to 110		1.3950			.698 to .700.		
2,5-Me$_2$Hexane [6, 7, 8, 9]	107.5 to 109.2.		1.3922 to 1.3932.		−91.3	.693 to .698.		
3,3-Me$_2$Hexane [7]	111 to 112		1.3998			.7116		
2,2,3-Me$_3$Pentane [6, 10]	110.2 to 110.8.		1.4030			.7173		

The material in the next higher-boiling cut was subjected to successive fractionations, the last of which yielded data given in figure 13. The constant-boiling fractions were combined, as were the four fractions near the peak of the refractive-index curve. Two successive crystallizations from methane increased the diversity in characteristics of these two batches of material, proving the presence of at least two compounds. Properties of the final preparations designated as materials 2.3422CC and 2.3424CC, are given, with comparison data, in table 5, and their distillations are shown in figures 14 and 15.

TABLE 5.—*Properties of compounds boiling near 114° C*

Material	Boiling point, 760 mm Hg	dt/dP	Refractive index		Freezing point	Density D/20	dD/dt	ASTM octane number
			n_D^{20}	n_D^{25}				
	°C	°C/mm Hg			°C	g/ml	g/ml/°C	
2.3422CC	113.89	0.0484	1.40475	1.40263	−122.12	0.7200	0.00084	97.7
2.3424CC	114.64		1.40661	1.40447	−114.83	.7249	.00089	99.1
2,3,4-Me$_3$Pentane [10]	112.8		1.4045			.7197		
2,3,3-Me$_3$Pentane [10]	113.6		1.4074			.7258		
2,3-Me$_2$Hexane [6]	114		1.4095			.719		

Nearly one-fourth of the residue distilled between 120 and 130° C. Two fractional distillations separated this material into two compounds, one boiling at 124° C and one at 126° C. A third distillation of the 124° C material yielded fractions the freezing points of which are shown in figure 16. This material is characterized by an increasing propensity to subcool as its purity is increased. A freezing curve on the purest fraction is shown in figure 17. The 126° C material was twice crystallized from methane. Properties of the purest preparations of these two materials, designated as 2.422 and 2.52CC, are given in table 6, together with the properties found in the literature for 2,2,5-trimethylhexane. Distillation curves of the two materials are given in figures 18 and 19.

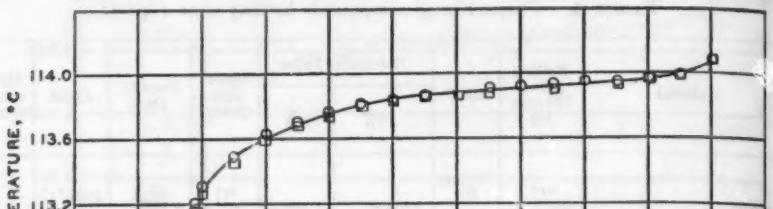

FIGURE 14.—*Distillations of a purified octane, probably 2,3,4-trimethylpentane.*

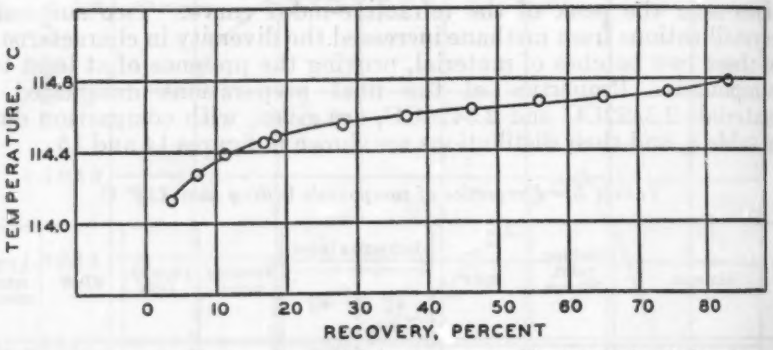

FIGURE 15.—*Distillation of a purified octane, probably 2,3,3-trimethylpentane.*

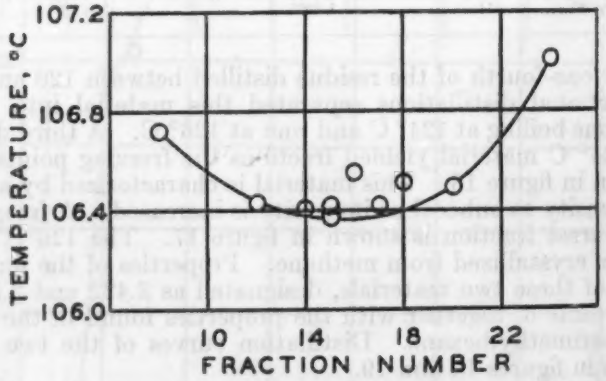

FIGURE 16.—*Freezing points of fractions of purified 2,2,5-trimethylhexane.*

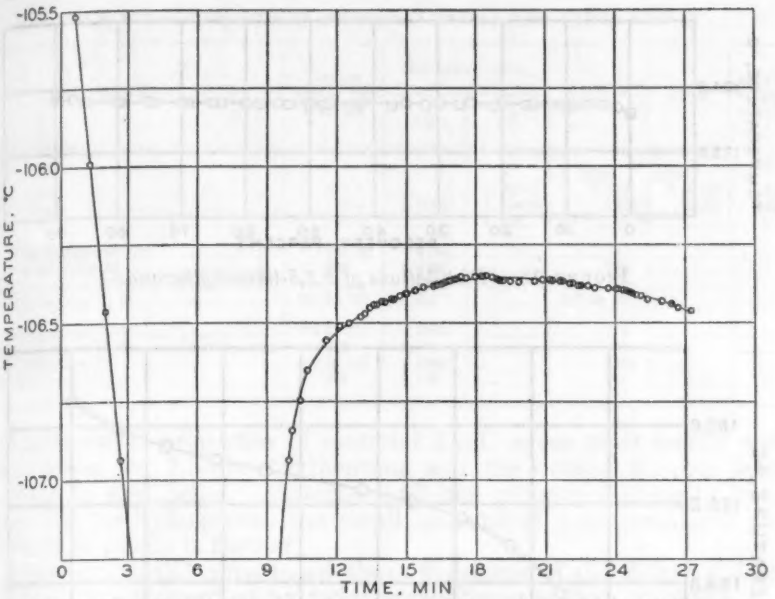

FIGURE 17.—*Freezing curve of purest fraction of 2,2,5-trimethylhexane.*

TABLE 6.—*Properties of compounds boiling near 125° C*

Material	Boiling point, 760 mm Hg	dt/dP	Refractive index		Freezing point	Density $D/20$	dD/dt	ASTM Octane number
			n_D^{20}	n_D^{25}				
	°C	°C/mm Hg			°C	g/ml	g/ml/°C	
2.422	124.09	0.0492	1.39967	1.39736	−106.35	0.70755	0.000805	91.2
2.52CC	126.51	.0491	1.40312	1.40097	−129.53	.7048	.00083	92.1
2,2,5-Me$_3$Hexane [7, 11]	121 to 123 126		1.3997			.70911		

A cryoscopic determination with benzene as the solvent gave 128.0 for the molecular weight of the 2.422 material. By analogy with properties given in the literature for 2,2,3-trimethylbutane, 2,2,4-trimethylpentane, and 2,2,6-trimethylheptane, it is clear that material 2.422 is 2,2,5-trimethylhexane, although the data given in the literature for the latter compound apparently were obtained on preparations of low purity. The 2.52CC material is, in view of its boiling point and octane number, probably a trimethylhexane. This is supported by the close agreement of its physical properties with those of the 2.422 material. Of the trimethylhexanes it seems probable that the 2,2,4-isomer would have properties most like those found for the 2.52CC material.

Small amounts of materials boiling between 132 and 142° C were obtained from the Röhm & Haas residue. None of these materials could be purified sufficiently to obtain a freezing point, although two were crystallized once from methane. The measured properties of the 2.54C material, given in table 7, agree reasonably with those given for 2,3,5-trimethylhexane, but its octane number, 66.9, is so low that it seems more likely that it may be 2,4-dimethylheptane.

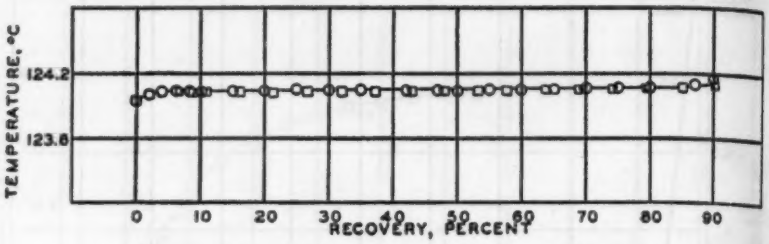

FIGURE 18.—*Distillations of 2,2,5-trimethylhexane.*

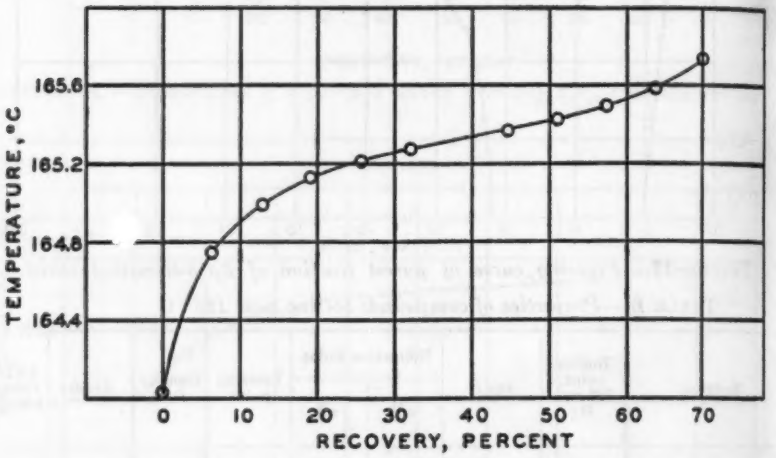

FIGURE 19.—*Distillations of a purified nonane, probably a trimethylhexane.*

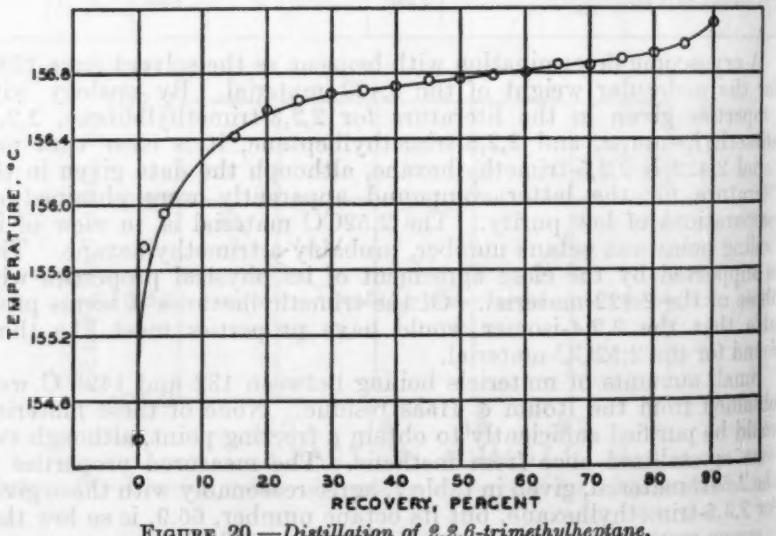

FIGURE 20.—*Distillation of 2,2,6-trimethylheptane.*

TABLE 7.—*Properties of compounds boiling from 132 to 142° C*

Material	Boiling point, 760 mm Hg	Refractive index		Density $D/20$	dD/dt	ASTM octane number
		n_D^{20}	n_D^{25}			
	° C			g/ml	g/ml/° C	
2.54C	132.1	----------	1.40305	0.7188	0.00088	66.9
2.62C	135.9	1.40664	1.40455	.7224	.00082	49.4
2.63	141.4	----------	1.4124	.738	----------	----------
3,3-Me$_2$-3-EtPentane [12]	141.60	1.4186	----------	----------	----------	----------
2,3,5-Me$_3$Hexane [8]	130	1.4051	----------	.716	----------	----------
2,3-Me$_2$Heptane [12]	140.6	1.4085	----------	.7235	----------	----------
2,4-Me$_2$Heptane [7, 8]	131 to 133	1.403	----------	.712 to .733	----------	----------
2,5-Me$_2$Heptane [7, 8]	133 to 137	1.4033	----------	.714	----------	----------
2,6-Me$_2$Heptane [5, 6]	132	1.401	----------	.707	----------	----------
3,3-Me$_2$Heptane [7]	137 to 138	1.4095	----------	.7304	----------	----------
4-EtHeptane [16]	139	1.408	----------	.741	----------	----------

The physical properties of material 2.62C agree most nearly with those given for 3,3-dimethylheptane and the octane number lends support to this belief. Material 2.63 has properties close to those given for 4-ethylheptane; the small amount of 2.63 precluded any attempt to purify it further.

Material 2.65CC constituted about 6 percent of the Röhm & Haas residue. It was purified by twice crystallizing it from methane.

TABLE 8.—*Properties of compounds boiling near 150° C*

Material	Boiling point, 760 mm Hg	dt/dP	Refractive index		Freezing point	Density $D/20$	dD/dt	ASTM octane number
			n_D^{20}	n_D^{25}				
	° C	° C/mm Hg			° C	g/ml	g/ml/C	
2.65CC	148.93	0.0510	1.40777	1.40560	−105.0	0.7238	0.00087	78.7
2.68C	151.97	.0540	1.41278	1.41076	----------	.7349	----------	80.5
2.72C-1	156.77	----------	1.41353	1.41151	----------	.7374	.00081	53.2
2,2,6-Me$_3$Heptane [11]	151 to 152	----------	1.4090	----------	----------	.7215	----------	----------
2,4-Me$_2$Octane [8]	153.5	----------	1.4090	----------	----------	.725	----------	----------
2,6-Me$_2$Octane [6]	159 to 160.5	----------	1.411	----------	----------	.734	----------	----------

Comparing the properties of this material with the listed properties, table 8, of 2,2,6-trimethylheptane, and with additional properties extrapolated from those of the analogous isomers of fewer carbon atoms (sometimes referred to as the 2,2,2′-isomers), it seems certain that material 2.65CC is 2,2,6-trimethylheptane, although much purer than previous preparations. The distillation curve, figure 20, by analogy with those for similar materials of known purity, suggests that this material is about 98 percent pure.

A much small quantity of material 2.68C was recovered from the source material, and was crystallized from methane once. The properties of this preparation are given in table 8 and the distillation data in figure 21. No compound listed in the available literature shows similar properties. From the octane number it appears likely to be a trimethylheptane; the similarity between the respective properties of this material and 2,2,6-trimethylheptane, and of material 2.52CC and 2,2,5-trimethylhexane, suggests that 2.68C may be 2,2,4- or 2,2,5-trimethylheptane, although this is definitely speculative.

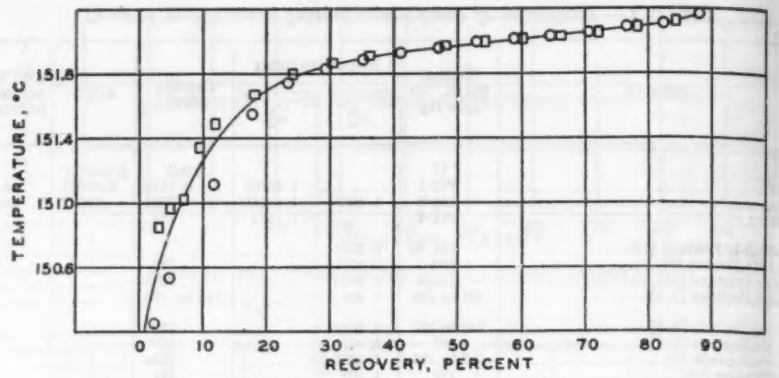

FIGURE 21.—*Distillations of a purified decane, probably a trimethylheptane.*

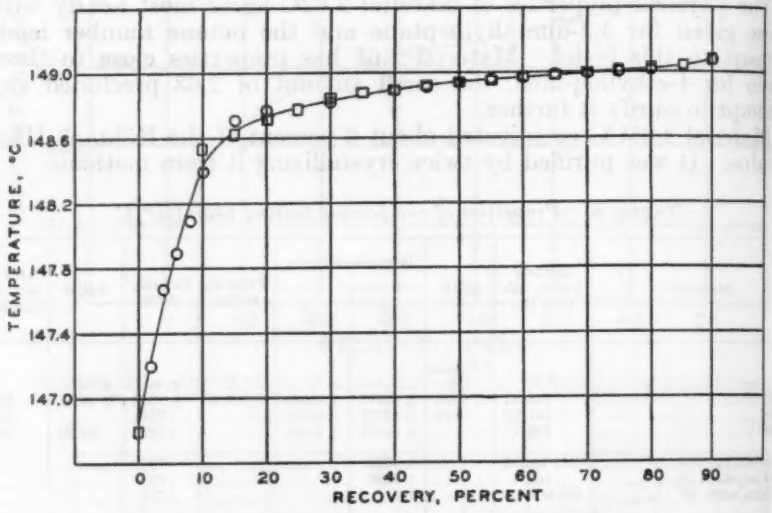

FIGURE 22.—*Distillation of a purified decane, unidentified.*

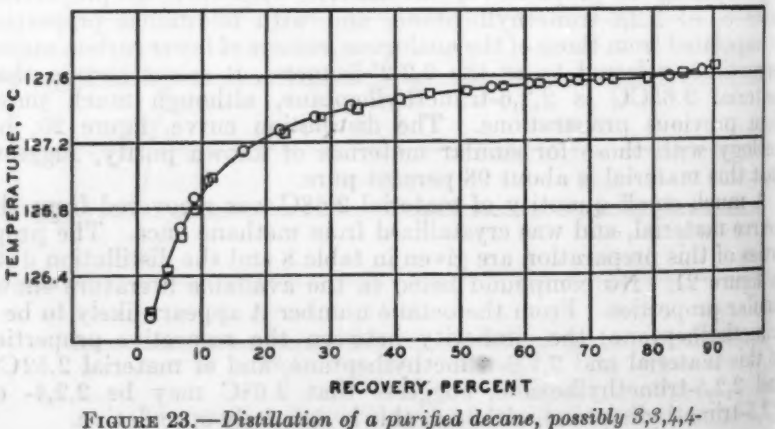

FIGURE 23.—*Distillation of a purified decane, possibly 3,3,4,4-tetramethylhexane.*

Material 2.72C–1, the properties of which are given also in table 8, and the distillation in figure 22, cannot be identified even tentatively, although its properties are close to those given for 2,6-dimethyloctane.

Materials 2.72C–2 and 2.74, the properties of which are given among those in table 9 and the distillation data in figures 23 and 24 are possibly the same material in different states of purity. These materials may be 3,3,4,4-tetramethylhexane.

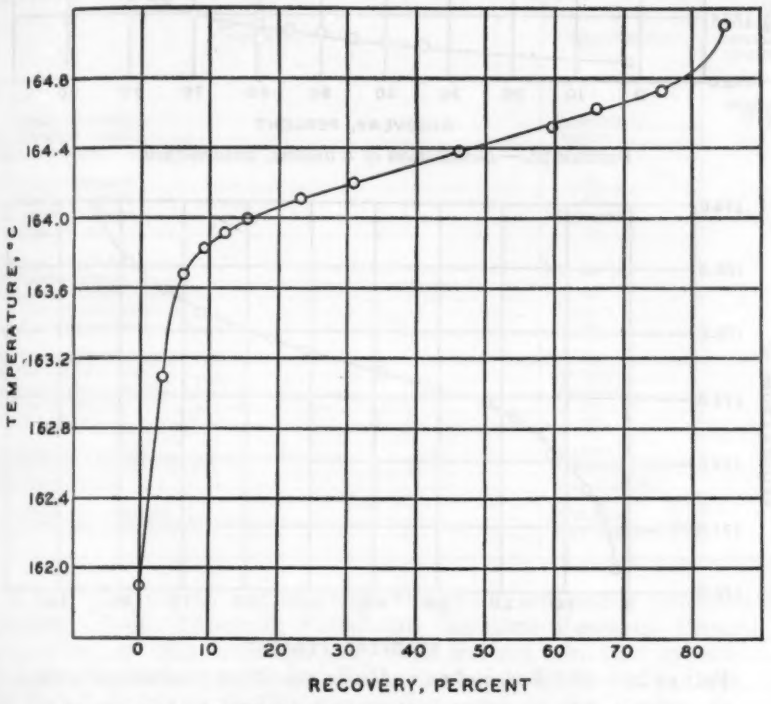

FIGURE 24.—*Distillation of a purified decane, possibly 3,3,4,4-tetramethylhexane.*

TABLE 9.—*Properties of compounds boiling above 160° C*

Materials	Boiling point, 760 mm Hg	Refractive index		Density $D/20$	dD/dt	ASTM octane number
		n_D^{20}	n_D^{25}			
	°C			g/ml	g/ml/° C	
2.72C–2	165.42	1.42161	1.41956	0.7538	0.00081	69.2
2.74C	164.42	1.42229	1.42029	.7565	.00080	65.4
2.76	172.28	1.4161	1.4138	.7430	.00070	68.4
2.78	178.06		1.4258	.7580	.00073	86.0
2.82C	182.76	1.42333	1.42130	.7539	.00074	78.4
3,3,4,4-Me_4Hexane [13]	163.5			.7608		
2,3,7-Me_3Octane [8]	175			.756		

The remaining materials listed in table 9 were obtained in small quantities, and, with the exception of 2.82C, would not crystallize from methane. Distillation curves for materials 2.76, 2.78, and 2.82C are given in figures 25, 26, and 27. These materials have not

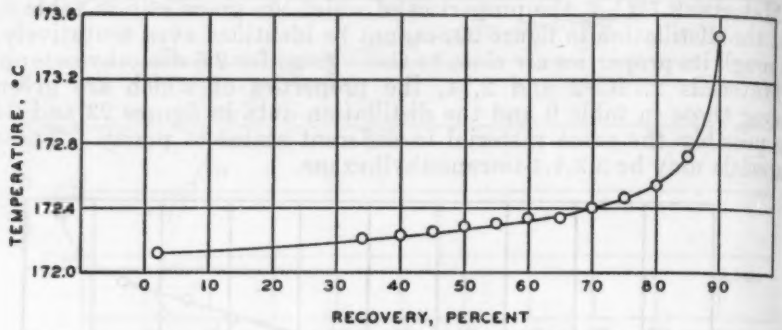

FIGURE 25.—*Distillation of a decane, unidentified.*

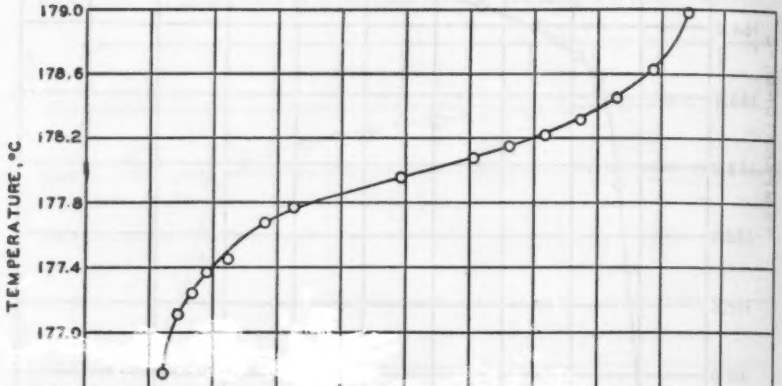

FIGURE 26.—*Distillation of an undecane, possibly a pentamethylhexane.*

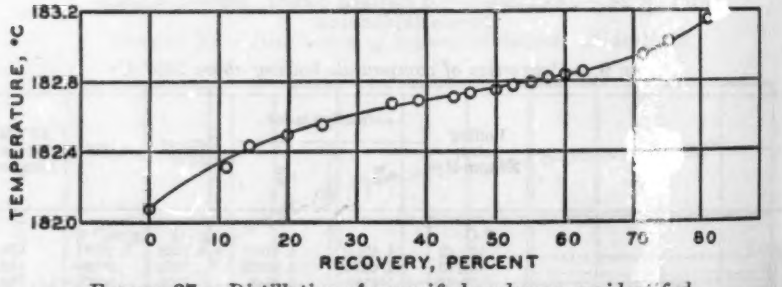

FIGURE 27.—*Distillation of a purified undecane, unidentified.*

been identified. Material 2.78, which from its boiling point must be an undecane, appears to have a highly branched chain, in view of its octane number. Its properties do not suggest the hexamethylpentane, but it is possibly one of the pentamethylhexanes, such as the 2,2,3,3,4-isomer. For a compound of so high a boiling point, this material has an unusually high octane number.

VI. SUMMARY

In conclusion, the compounds listed in table 10 have been isolated from the crude synthetic isooctane, and have been identified with the degree of certainty indicated.

TABLE 10.—*Summary of compounds isolated*

Compound	Identification	Percentage present in crude
		Percent
2,2-Dimethylbutane	Probable	0.01
2,3-Dimethylbutane	Positive	.03
2-Methylpentane	do	.02
2,3-Dimethylpentane	do	.19
2,4-Dimethylpentane	do	.03
2,3-Dimethylpentane	Probable	.01
2-Methylhexane	do	.02
2,4-Dimethylhexane	do	.04
2,5-Dimethylhexane		
3,3-Dimethylhexane	do	.04
2,3,4-Trimethylpentane	Positive	.12
2,3,3-Trimethylpentane	do	.10
2,2,5-Trimethylhexane	do	.50
2,2,4-Trimethylhexane	Probable	.10
2,4-Dimethylheptane	Doubtful	.03
3,3-Dimethylheptane	do	.04
4-Ethylheptane	do	.01
2,2,6-Trimethylheptane	Positive	.13
2,2,4- or 2,2,5-Trimethylheptane	Probable	.02
2,6-Dimethyloctane	Very doubtful	.02
3,3,4,4-Tetramethylhexane	Probable	.04
2,2,3,3,4-Pentamethylhexane	Very doubtful	.02

It is a pleasure to acknowledge the great assistance rendered by members of the American Petroleum Institute Research Project 6, in carrying out this investigation. The writers take this opportunity to express indebtedness to Dr. F. D. Rossini and Mr. F. W. Rose, Jr., for their help given in this connection, and to the Project for the use of their distillation apparatus.

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WASHINGTON, July 21, 1937.

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HEATS OF COMBUSTION AND OF FORMATION OF THE NORMAL OLEFIN (ALKENE-1) HYDROCARBONS IN THE GASEOUS STATE

By Frederick D. Rossini and John W. Knowlton

ABSTRACT

The existing thermochemical data on the normal olefin (alkene-1) hydrocarbons are reviewed and correlated. These data are used in conjunction with the value previously proposed for the increase in the heat content per added CH_2 group to obtain values for those members of this series of hydrocarbons for which no calorimetric data exist. For all these hydrocarbons in the gaseous state, selected "best" values are given for the heats of combustion at 25°C and for the heats of formation, from solid carbon and gaseous hydrogen, at 25°C and 0°K.

As in the case of the previously reported values for the normal paraffin hydrocarbons and primary normal alkyl alcohols, the heats of formation of the gaseous normal olefin (alkene-1) hydrocarbons can be represented by means of an expression of the form $\Delta H = A + Bn + \Delta$, where ΔH is the heat of formation, A and B are constant for a given temperature, n is the number of carbon atoms in the molecule C_nH_{2n}, and Δ is the term giving the deviation from linearity, which is zero for $n > 5$. Values of the constants A and B and of Δ are given both for 25° C and 0° K.

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I. INTRODUCTION

The purpose of the present paper is to deduce reliable values for the heats of combustion and of formation of all the normal olefin (alkene-1) hydrocarbons in the gaseous state by using the following: (1) the generalization recently made by one of the authors [1] [1] that, in any organic molecule containing a normal alkyl group of more than five carbon atoms, the addition of a CH_2 group to the normal alkyl radical to form the next higher normal alkyl group results in an increase in the heat of combustion of the organic molecule in the gaseous state, at a temperature of 25° C and a constant total pressure of 1 atmosphere, of 157.00 ± 0.08 kilocalories per mole; (2) the heats of combustion of ethylene and propylene recently measured in this laboratory [2]; (3) the heats of hydrogenation of ethylene, propylene, normal butene-1, and normal heptene-1 recently reported by Kistiakowsky, Vaughan, et al. [3, 4]; and (4) the heats of combustion of hydrogen and of the gaseous normal paraffin hydrocarbons as reported from this laboratory [5, 1].

[1] The numbers in brackets here and throughout the text refer to the references at the end of the paper.

II. UNITS OF ENERGY AND MOLECULAR WEIGHTS

The values of energy given in this paper are based upon the international joule as derived from standards maintained at this Bureau. As in previous papers, the following conversion factor [6] is used for reporting the results in terms of the defined calorie:

1 NBS international joule=1/4.1833 calorie.

The establishment of the uncertainties attached to the various values presented in this paper follows the procedure described in reference [6].

It is to be emphasized that the molal units of mass associated with the values given for the heats of combustion represent true moles well within the limits of uncertainty of the selected values because (1) the experimental values of heats of combustion are entirely independent of the atomic weight of carbon, the number of moles of hydrocarbon being determined from the mass of H_2O formed in the combustion [1, 8], and (2) the relatively small values of heats of hydrogenation are expressed in terms of moles as determined from the mass of CO_2, so that in this latter case the atomic weight of carbon enters as only 12/44 and can make only a negligible absolute error in the energy value finally deduced. For the heats of formation, a little greater uncertainty [1] is introduced because the existing data for the heat of formation of carbon dioxide from its elements are based upon the mass of carbon burned, and consequently the values carry the full uncertainty in the value for the atomic weight of carbon, in addition to the calorimetric and thermodynamic uncertainties.

III. EXISTING DATA

The existing data on the heats of combustion of ethylene and propylene have already been reviewed [2, 7].

"Calculated" values for the heats of combustion of ethylene and propylene have also been derived by the authors [2] using values for the heats of combustion of hydrogen, ethane, and propane obtained in this laboratory [5, 8] and values for the heats of hydrogenation of ethylene and propylene obtained at Harvard University [3, 4]:

$$C_nH_{2n+2}(g)+\frac{3n+1}{2}O_2(g)=nCO_2(g)+(n+1)H_2O(liq) \quad (1)$$

$$(n+1)H_2(g)+\frac{n+1}{2}O_2(g)=(n+1)H_2O(liq) \quad (2)$$

$$C_nH_{2n}(g)+H_2(g)=C_nH_{2n+2}(g) \quad (3)$$

The sum of reactions (1) and (3), less reaction (2), yields the reaction for the combustion of the olefin hydrocarbon:

$$C_nH_{2n}(g)+\frac{3n}{2}O_2(g)=nCO_2(g)+nH_2O(liq) \quad (4)$$

In a manner similar to that above, there can be obtained "calculated" values for the heats of combustion of gaseous normal butene-1 and gaseous normal heptene-1, using the following data: for the heats of combustion of normal butane and normal heptane, according to reaction (1), $-\Delta H=2877.88\pm0.63$ and 4850.12 ± 2.34 inter-

national kilojoules, or 687.94±0.15 and 1159.40±0.56 kilocalories per mole, respectively, at 25° C and 1 atmosphere [8, 1]; for the heat of formation of liquid water, according to reaction (2), $-\Delta H=285.775\pm0.040$ international kilojoules, or 68.313±0.010 kilocalories per mole at 25° C and 1 atmosphere [5]; and for the heats of hydrogenation of normal butene-1 and normal heptene-1, according to reaction (3), $-\Delta H=125.62\pm0.32$ and 124.75 ± 0.32 international kilojoules or 30.03±0.08 and 29.82±0.08 kilocalories per mole at 25° C and 1 atmosphere. These latter values are derived from the experimentally determined ones for 82° C [4] by using for reaction (3) the relation

$$\Delta H_{355}-\Delta H_{298}=-0.321\pm0.040 \text{ kilocalories per mole} \quad (5)$$

which has been calculated by Kassel [17, 18].

From the value thus calculated for the heat of combustion of gaseous normal heptene-1, which should be a reliable one judging from the accord previously found between the "calculated" and experimental values for ethylene and propylene [2], there can be derived values for the heats of combustion of all the normal olefin (alkene-1) hydrocarbons above heptene by using the generalization mentioned in the introduction of this paper [1]. In this manner, there is obtained for the reaction

$$C_nH_{2n}\,(g)+\frac{3n}{2}\,O_2(g)=n\,CO_2(g)+n\,H_2O(liq) \quad (6)$$

with $n>5$, for 25° C and 1 atmosphere,

$$-\Delta H=178.90+157.00(n-1) \text{ kilocalories per mole} \quad (7)$$

with an uncertainty of about ± (0.10n−0.10) kilocalories per mole, where n is the number of carbon atoms per molecule.

There is reported in the literature one value for the heat of combustion of "amylene" and one for "hexylene", the latter being carried out in a bomb at constant volume. The former was reported by Favre and Silbermann [9] in 1852 and the latter by Zubow [10, 11] in 1898. Because of the uncertainty as to the purity and isomeric form of the actual material burned and as to the unit of energy of these early experiments, these two values are considered to be of historical interest only.

The experimental values for ethylene and propylene, and the "calculated" values for ethylene, propylene, normal butene-1, normal heptene-1, and the normal olefins (alkene-1) above heptene, are shown in figure 1. By interpolation on this chart, reliable values are obtained for normal pentene-1 and normal hexene-1, of which neither the heat of combustion nor of hydrogenation has ever been measured experimentally.

IV. SELECTED "BEST" VALUES FOR THE HEATS OF COMBUSTION AT 25° C

From the values given by the curve in figure 1, the selected "best" values given in table 1 are obtained for the heats of combustion of all the normal olefin (alkene-1) hydrocarbons in the gaseous state at 25° C and 1 atmosphere, according to reaction (4). For $n>5$, the

following linear relation (see page 341) holds for reaction (6) at 25° C and 1 atmosphere:

$$-\Delta H = 21.90 + 157.00n \pm (0.10n - 0.10) \text{ kilocalories per mole} \quad (8)$$

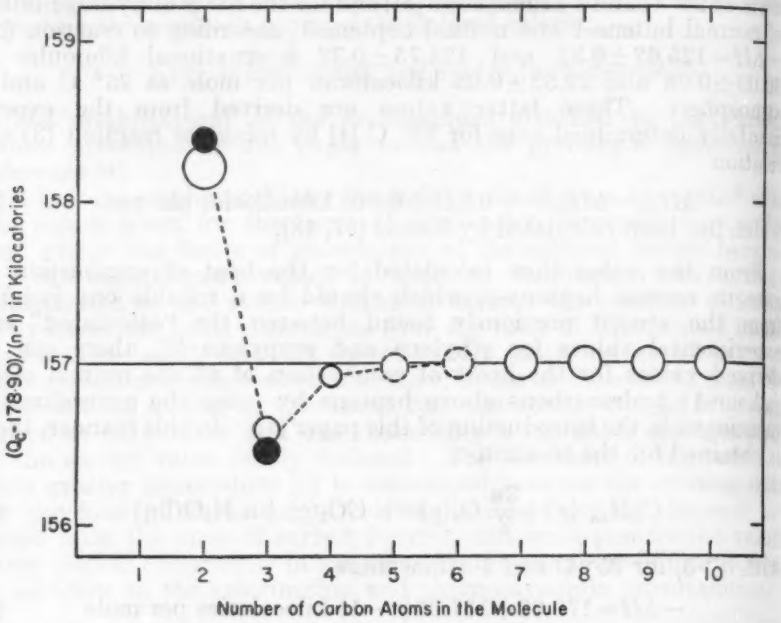

FIGURE 1.—*Relation between the heats of combustion of the gaseous normal olefin (alkene-1) hydrocarbons and the number of carbon atoms in the molecule.*

The scale of ordinates gives the function $(Qc-178.90)/(n-1)$, where Qc is the heat of combustion of the gaseous olefin at 25° C and a constant total pressure of 1 atmosphere, in kilocalories per mole, and n is the number of carbon atoms in the molecule. The scale of abscissas gives the number of carbon atoms in the molecule. The solid black circles represent directly measured values [2]; the open circles represent calculated values (see p. 341); the broken circles represent interpolated values. The radii of the various circles represent the estimated uncertainties.

TABLE 1.—*Selected "best" values for the heats of combustion of the gaseous normal olefin (alkene-1) hydrocarbons at 25° C*

$$C_nH_{2n}(g) + \frac{3n}{2}O_2(g) = nCO_2(g) + nH_2O(liq)$$

C_nH_{2n}(gas)	$-\Delta H$ at 25° C and 1 atm
	Kilocalories per mole [1]
Ethylene	337.25±0.07.
Propylene	491.90±0.15.
Normal butene-1	649.66±0.18.
Normal pentene-1	806.78±0.32.
Normal hexene-1	963.90±0.45.
Normal heptene-1	1,120.90±0.60.
Normal octene-1	1,277.90±0.70.
Normal nonene-1	1,434.90±0.80.
Normal decene-1	1,591.90±0.90.
Normal C_nH_{2n} (for $n>5$)	$21.90+157.00n\pm(0.10n-0.10)$.

[1] See p. 340 for unit of energy and molecular weights.

V. HEATS OF FORMATION AT 25° C AND 0° K

By combining the reaction of combustion as given by equation 4 with the heats of formation of water and of carbon dioxide from their elements, there is obtained the reaction of forming the hydrocarbon

from its elements. The value for the heat of formation of water according to reaction (2) has already been given. For the heat of formation of carbon dioxide from its elements,

$$C\ (c,\ graphite)+O_2(g)=CO_2(g), \tag{9}$$

$$C\ (c,\ diamond)+O_2(g)=CO_2(g), \tag{10}$$

a previous review of the existing data [1] yielded, for reaction (9), $-\Delta H=94.20\pm0.08$ kilocalories per mole at 25° C and 1 atmosphere, where the amount of reaction was determined from the mass of carbon and 1 gram-atom of carbon was taken as 12.007 ± 0.003 g. The International Committee on Atomic Weights this year [16] changed the value for the atomic weight of carbon from 12.00 to 12.01. The available data indicate rather definitely that the uncertainty in the new value cannot be more than about 0.003. Taking 1 mole of carbon dioxide as given by 12.010 ± 0.003 g of carbon, the value for the heat of reaction (9) becomes $-\Delta H=94.22\pm0.08$ kilocalories per mole at 25° C and 1 atmosphere. Since this value is still substantially the same as the old one, 94.24 (see [1]), the values already used [1] for reactions (9) and (10), namely, $-\Delta H=94.24\pm0.10$ and 94.46 ± 0.10 kilocalories per mole, respectively, at 25° C and 1 atmosphere, will be used in the present calculations.

With the foregoing values for the heats of formation of water and carbon dioxide and the values for the heats of combustion given in table 1, there are obtained the values for the heats of formation of the gaseous normal olefin (alkene-1) hydrocarbons at 25° C as given in table 2.

For the reaction

$$nC\ (c,\ graphite)+nH_2(g)=C_nH_{2n}(g) \tag{11}$$

$$\Delta H^\circ_{298.16}=21.90-5.55_3n+\Delta\pm(0.14n-0.06),\ \text{kilocalories per mole}, \tag{12}$$

where $\Delta=0$ for $n>5$, and has the following values for $n\leq5$: ethylene, 1.35 ± 0.07; propylene, -1.00 ± 0.15; normal butene-1, -0.24 ± 0.18; normal pentene-1, -0.12 ± 0.32, kilocalories per mole.

For the reaction

$$nC\ (c,\ diamond)+nH_2(g)=C_nH_{2n}(g) \tag{13}$$

$$\Delta H^\circ_{298.16}=21.90-5.77_3n+\Delta\pm(0.14n-0.06)\ \text{kilocalories per mole}, \tag{14}$$

where Δ has the same values as above.

TABLE 2.—*Heats of formation of the gaseous normal olefin (alkene-1) hydrocarbons, from solid carbon and gaseous hydrogen at 25° C and 0° K*

$C_nH_{2n}(g)$	$nC\ (c,\ graphite)+nH_2(g)=C_nH_{2n}(g)$		$nC\ (c,\ diamond)+nH_2(g)=C_nH_{2n}(g)$	
	$\Delta H^\circ_{298.16}$	ΔH°_0	$\Delta H^\circ_{298.16}$	ΔH°_0
	Kilocalories per Mole	*Kilocalories per Mole*	*Kilocalories per Mole*	*Kilocalories per Mole*
Ethylene	12.14 ± 0.21	14.16 ± 0.21	11.70 ± 0.21	13.47 ± 0.21
Propylene	4.24 ± 0.34	7.61 ± 0.35	3.58 ± 0.34	6.57 ± 0.35
Normal butene-1	-0.55 ± 0.44	4.33 ± 0.46	-1.43 ± 0.44	2.95 ± 0.46
Normal pentene-1	-5.99 ± 0.60	0.42 ± 0.63	-7.09 ± 0.60	-1.31 ± 0.63
Normal hexene-1	-11.42 ± 0.76	-3.49 ± 0.79	-12.74 ± 0.76	-5.57 ± 0.79
Normal heptene-1	-16.97 ± 0.92	-7.53 ± 0.98	-18.51 ± 0.92	-9.95 ± 0.98
Normal octene-1	-22.52 ± 1.06	-11.56 ± 1.17	-24.28 ± 1.06	-14.33 ± 1.17
Normal nonene-1	-28.08 ± 1.20	-15.59 ± 1.36	-30.06 ± 1.20	-18.71 ± 1.36
Normal decene-1	-33.63 ± 1.34	-19.63 ± 1.55	-35.83 ± 1.34	-23.09 ± 1.55
Normal C_nH_{2n} (for $n>5$)	$21.90-5.55_3n\pm(0.14n-0.06)$	$20.71-4.03_8n\pm(0.19n-0.35)$	$21.90-5.77_3n\pm(0.14n-0.06)$	$20.71-4.37_8n\pm(0.19n-0.35)$

NOTE.—The estimated uncertainties given here represent the absolute error in each of the values. The uncertainty in the difference between any two values in a given column is about $\pm0.14\Delta n$ at 25° C and $\pm0.19\Delta n$ at 0° K.

In order to calculate the corresponding heats of formation at 0° K, it is necessary to know the value of $H^\circ_{298.16}-H^\circ_0$ for the hydrocarbon, hydrogen, diamond, and graphite. Values for the latter three substances as given in the previous publication [1] are, respectively, 2.023 ± 0.001, 0.125 ± 0.013, and 0.251 ± 0.006 kilocalories per mole. For ethylene, the values may be taken from the calculations of Smith and Vaughan [19] as 2.534 ± 0.030 kilocalories per mole. For the members of the series above ethylene, Kassel [17, 18] has estimated that the value is 0.254 kilocalories per mole less than that of the corresponding paraffin. By combining this with the equation previously given by Kassel for the normal paraffin hydrocarbons [1], there is obtained for the gaseous normal olefin (alkene-1) hydrocarbons,

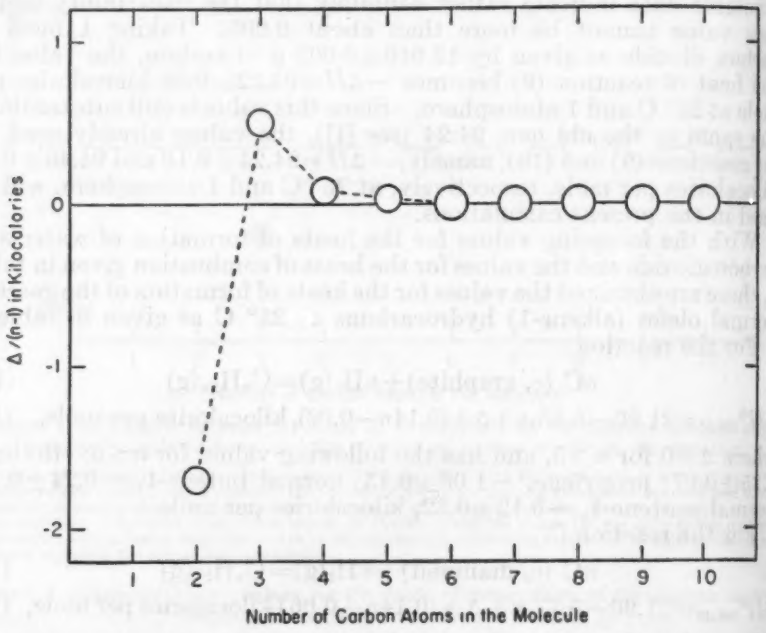

FIGURE 2.—*Plot of the deviations from linearity in the relation between the number of carbon atoms in the normal olefin (alkene-1) molecule and its energy of dissociation into normal atoms, at 0° K.*

The scale of ordinates gives the value of $\Delta/(n-1)$, where Δ is the deviation from linearity in kilocalories per mole and n is the number of carbon atoms in the molecule. The scale of abscissas gives the number of carbon atoms in the molecule.

C_nH_{2n}, with $n>2$, $H^\circ_{298.16}-H^\circ_0=1.191+0.754n$ $(1\pm0.01n)$ kilocalories per mole.

With these values for the increase in heat content of the various molecules in going from 0° K to 298.16° K (25° C), there are obtained the values given in table 2 for the heats of formation at 0° K.

For the reaction

$$nC(c, \text{graphite})+nH_2(g)=C_nH_{2n}(g) \tag{15}$$

$$\Delta H^\circ_0=20.71-4.03_3n+\Delta\pm(0.19n-0.35) \text{ kilocalories per mole,} \tag{16}$$

where $\Delta=0$ for $n>5$, and for $n\leqq5$ has the same values as at 25° C (equation 1) except for ethylene, for which the value of Δ is 1.52 ± 0.08 kilocalories per mole.

For the reaction

$$nC(c, \text{diamond})+nH_2(g)=C_nH_{2n}\ (g)$$

$$\Delta H_0^\circ=20.71-4.37_9n+\Delta\pm(0.19n-0.35)\ \text{kilocalories per mole,} \quad (17)$$

where Δ has the same values as for equation 16.

In figure 2 is shown the relation between the number of carbon atoms in the molecule and the deviation from linearity in the energy of dissociation [1, 12] of the normal olefin (alkene-1) hydrocarbon into normal gaseous carbon and hydrogen atoms, at 0° K, according to the reaction

$$C_nH_{2n}\ (g)=n\ C(g)+2n\ H(g) \quad (18)$$

The deviation, Δ, is plotted as the function $\Delta/(n-1)$ against n, the number of carbon atoms in the molecule. Δ has the following values at 0° K: ethylene, -1.52 ± 0.08; propylene, $1.00\ \pm0.16$; normal butene-1, 0.24 ± 0.24; normal pentene-1, 0.12 ± 0.36; $n>5$, $0.00\pm(0.10n-0.10)$ kilocalories per mole. It is to be noted that the deviations from linearity are all in the direction of greater energy of dissociation of the molecule, except for ethylene, which is in the direction of lesser energy of dissociation.

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MEASUREMENTS OF CERTAIN PHYSICOCHEMICAL CONSTANTS OF BENZENE

By Mieczysław Wojciechowski [1]

ABSTRACT

A series of preparations of benzene of a high degree of purity were made by fractional distillation, by azeotropic distillation with ethanol, and by crystallization followed by centrifuging. The following physicochemical constants were measured: boiling point, 80.094 ±0.002° C; freezing point, 5.51 ±0.01° C; refractive index n_D^{25}, 1.49807 ±0.00006; and density at 25° C, 0.87366 g/cm³ ±0.00002. Previous determinations of these constants, as reported in the literature, are reviewed.

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I. INTRODUCTION

Many authors have measured the physicochemical constants of benzene. Determinations of its boiling point were published in the year 1895 by E. Beckmann and G. Fuchs [1][2] and in 1898 by G. Kahlbaum [2]. The large difference between the results of these authors led B. Woringer [3] to carry out another determination. In 1910 Sydney Young [4] measured the boiling point (80.20° C) and density of benzene, and for many years his data were considered as the most reliable. In 1926 J. Timmermans and F. Martin [5] measured the boiling and freezing points, refractive index, and density of benzene, confirming the data reported by Young. However, the data published by A. Zmaczynski [6] in 1930, which were obtained by the comparative method of measurement with modern ebulliometers of the Świętosławski type, indicated that the accepted boiling point of benzene was in error. Later, this author published a second paper [7] reporting the boiling point of benzene as 80.110° C, a value 0.012° lower than that given in his first paper. This exceeds the possible error of the temperature determination by the comparative method, the difference being caused, probably, by a difference in the purity of the preparations investigated.

Benzene is a very important substance and may prove suitable as a standard for some physicochemical measurements. For example, there is need for stable liquids of high purity whose indices of refraction

[1] Guest worker, from Polytechnic Institute, Warsaw, Poland.
[2] The figures in brackets refer to references listed at the end of the paper.

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may be established to serve as standards supplementing water for the adjustment of refractometers. For this reason, it was desired to work out a reliable method for preparing it in a state of the highest purity as well as to redetermine the physicochemical constants, boiling and freezing points, refractive index, and density.

It is probable that many of the discrepancies of the results for physicochemical constants published by various authors have originated mainly in their attempts to carry out absolute measurements, instead of using the easier and more precise method of comparative measurements. In the present work emphasis was placed on careful purification by physical methods, of preparations previously purified by chemical means, and on proof that the final preparations were really of very high purity. Three different methods of purification were used, and as a result there were obtained several preparations which were tested for purity by the ebulliometric method [8] before the measurements of the physicochemical constants were made.

II. METHODS OF PURIFICATION

The initial material was a quantity of benzene which conformed to the specifications adopted by the American Chemical Society for this substance as an analytical reagent [9]. This material corresponded to the fifth degree of purity on the Świętosławski scale, the difference between its boiling and condensation temperatures being 0.005° C. Since the nature of the impurities in the initial substance was unknown and since by the aid of one method alone it would probably be impossible to remove all impurities, three different means of purification were applied.

For the purification of the benzene by the first method, 2 liters of the initial substance was fractionally distilled. A 40-bulb column of the Świętosławski type [10], with vacuum jacket, was used and adjusted so that the reflux ratio was 10 : 1 and the rate of distillation 20 ml per hour. In this distillation equal volumes of head and tailings were rejected and five middle fractions of 200 ml each were collected, labelled as preparations A: A_a, A_b, A_{I}, A_{II}, and A_{III}. Only fractions A_{I}, A_{II}, and A_{III} were used for the final measurement of properties.

The second portion was treated by crystallizing the benzene, centrifuging the mother liquor, and then distilling the crystal fraction. In this procedure, three liters of the initial preparation was used. The substance was cooled until about two-thirds of the total amount was crystallized. Then the crystals were crushed and the mother liquor removed from the mash, by the aid of a laboratory centrifuge constructed by R. T. Leslie and S. T. Schicktanz [11]. Next the crystals of benzene were melted and the liquid was distilled through the column. The fractions distilling at constant temperature within a limit of 0.001° were collected. By this procedure seven fractions of 200 ml each were obtained, designated as B_1 to B_7. The mother liquor was distilled separately until the same uniformity of boiling point was reached, and three fractions of 200 ml were retained, designated as C_{I} to C_{III}.

The third method was based on the azeotropic distillation of benzene with purified ethanol. Ethanol was then removed from the azeotropic mixture by washing out with water and the benzene distilled, only the middle fraction of the distillate being collected (preparation D). A binary mixture of ethanol and benzene boils at a much lower

temperature than pure benzene, and therefore higher-boiling impurities which do not form azeotropic mixtures with ethanol and benzene, such for instance as toluene, are easily removed. Only the middle fraction of the distillate, which distilled at practically constant temperature (±0.001° C), was collected for use. Then the benzene was separated from ethanol by the method of S. Young [12], by repeatedly washing out the alcohol with water. The preparation was finally distilled through the column to remove remaining minute quantities of ethanol and water.

III. INVESTIGATION OF THE DEGREE OF PURITY OF THE PREPARATIONS

Several criteria of purity were applied to the various preparations of benzene. The ebulliometric test of purity, based on the measurement of the difference Δt between the boiling point and the temperature of condensation in the differential ebulliometer of standardized dimensions of the Świętosławski type, indicated that all of the preparations were of a high degree of purity.

The second criterion of purity was the freezing behavior. Two of the fractions were frozen. In both cases the temperature of freezing was constant within 0.004° until approximately two-thirds of the material was solid. Beyond this point adequate stirring for proper heat exchange in the mixture of solid and liquid could not be obtained.

Another test of purity was the comparison of boiling points of the successive fractions of distillation, and those of the preparations purified by various methods.

IV. METHODS OF MEASUREMENT

Instead of the absolute measurements commonly used, which involve difficulties in calibrating apparatus, comparative measurements were employed for determining boiling point, density, and refractive index, using water as the reference liquid. The importance of comparative measurements to promote homogeneity of physicochemical data obtained in various laboratories has been emphasized in the literature by W. Świętosławski [14].

The methods and apparatus used were as follows:

1. Boiling points were determined by means of the comparative method of W. Świętosławski. For the measurements, a platinum resistance thermometer, constructed with a coiled filament designed by C. H. Meyers [15] and calibrated by the Heat Division of this Bureau, was used. The resistance of the thermometer was measured with a calibrated Mueller bridge. Measurements were reproduced within a precision of 0.001° C.

2. Freezing points were measured with an apparatus described by B. J. Mair [16]. The freezing tube, containing about 50 ml of benzene, was surrounded with an air jacket within an ice bath, for uniform cooling. A platinum resistance thermometer, the same that was used for measuring boiling points, was immersed in the freezing liquid. Stirring was done with a spiral surrounding the thermometer and moved up and down by an electric motor. Since water affects the freezing point of benzene, a current of dry air obtained by evaporation of liquid air was passed through the top of the tube, to avoid access of moisture. Somewhat more than two-thirds of each sample

was frozen during the measurements. The freezing point of the preparations was practically constant, since the changes of temperature did not exceed ±0.004° C, and the accuracy of the measurements is estimated to be within ±0.01°.

3. The measurements of density were made at 25° C by the comparative method with the use of twin silica pycnometers [17]. The value 0.997044 g/cm³ was used for the density of water at 25° C.

4. The refractive index for the sodium *D* lines was determined by means of a refractometer of the Abbe type, with the scale graduated to 0.0001, calibrated by the Optical Instruments Section of this Bureau. The determinations were made at 25° C. Water was used for adjusting the refractometer and the value of 1.33251 for its refractive index n_D^{25}, given in International Critical Tables, was taken. The accuracy of the measurements is believed to be ±0.00005.

V. EXPERIMENTAL RESULTS AND CONCLUSIONS

The results of all the measurements are given in table 1.

TABLE 1.—*Properties of the preparations of benzene*

Fraction	Δt	Normal boiling point	Freezing point	n_D^{25}	d_{25}
	°C	°C	°C		g/cm³
A_a				1.49810	
A_b				1.49812	
A_I	0.003	80.096		1.49811	0.87364
A_{II}	.002	80.097		1.49811	.87366
A_{III}	.002	80.097		1.49810	.87358
B_1	.002			1.49807	
B_2	.002	80.092		1.49804	.87367
B^3	.001	80.093		1.49804	.87365
B^4	.001	80.093	5.51	1.49804	.87366
B_5	.002	80.093		1.49804	.87366
B_6	.002	80.093		1.49806	.87367
B_7	.003	80.096		1.49804	.87373
C_I	.002	80.091		1.49802	.87366
C_{II}	.001	80.093	5.51	1.49809	.87368
C_{III}	.004	80.095		1.49809	.87361
D_1	.001	80.093		1.49802	.87367
Average		80.094	5.51	1.49807	.87366
Average deviation		±.002		±.00003	±.00002
Probable error		±.001		±.00001	±.00001

The middle fractions of benzene purified by crystallization and by distillation of the binary azeotropic mixture with ethanol had differences between the boiling point and temperature of condensation equal to 0.001° C. They had the same boiling point of 80.093° C. Their high purity is evident from the fact that a number of successive fractions of distillate had the same Δt and the same boiling point.

It is seen from table 1 that preparations *A* having Δt, the difference between the boiling point and condensation temperature, equal to 0.002° C, had the boiling point 80.097° C, whereas preparations with the same Δt, purified by the other methods, had a boiling point of 80.091 to 80.093° C. The preparations thus had a difference in boiling point of about 0.004°, although they had the same Δt. Since the standardized differential ebulliometer used for measuring the degree of purity has a rectifying efficiency equivalent to one theoretical plate [19], it cannot separate very minute amounts of impurities probably present in each preparation. These experiments show that when investigating preparations of extreme purity it is useful

to compare their boiling points, employing the measurements of Δt as a control to show that the preparation is really of the highest degree of purity on the Świętosławski scale.

However, in view of the high purity of the initial material ($\Delta t = 0.005°$), and its subsequent uniform improvement ($\Delta t = 0.001$ to $0.003°$) by each of the applied methods of purification, the averages of all determinations, without rejection of any single result or series, are taken for the final values of the measured properties.

The freezing curve was taken for the two middle fractions of the preparations *B* and *C*. In both cases, as already mentioned, more than two-thirds of the sample investigated crystallized practically at constant temperature. The freezing point of both preparations was the same within the limits of experimental error and was equal to 5.51° C.

Measurement of the refractive index has little significance as a criterion of purity of benzene, since this property is relatively insensitive to impurities but rather sensitive to changes of temperature. As an illustration, the following example may be reported. Benzene saturated with water at 25° C contains around 0.1 percent of water and has a refractive index lower by 0.00014 than benzene, water-free, whereas a change in temperature of 1° C causes a change in the refractive index n_D^{25} of 0.00063 [20]. From all of the measurements made, the refractive index of benzene at 25° C for the sodium line *D* may be taken as 1.49807 ± 0.00006.

The density of benzene at 25° C may be accepted as 0.87366 ± 0.00002 g/cm³, the average of all the data obtained.

For comparison of the values obtained in the present work with those previously reported, the data published by other authors are listed in table 2.

TABLE 2.—*Comparison of the results with the data published by other authors*

Author and reference no.	Boiling point	Freezing point	n_D^{25}	d_{25}
	°C	°C		g/cm³
E. Beckmann and G. Fuchs [1]	79.8			
G. Kahlbaum [2]	80.30			
B. Woringer [3]	79.43			
G. Dejardin [21]	80.15	5.58		
S. Young [4]	80.20			0.8738
A. Smith and A. Menzies [22]	80.15			
W. Atkins and F. Wallace [23]	80.08 to 80.12			
D. Tyrer [24]	80.28			
T. Richards and G. Shipley [25]	79.70 to 79.71			
J. Timmermans and F. Martin [5]	80.20	5.50	[a]1.50439	.87369
A. Zmaczynski [6, 7]	80.122 80.110			
J. Bruun and M. M. Hicks-Bruun [26]	80.1	5.3		
C. P. Smyth and W. S. Walls [27]	80.2 to 80.3		1.49815	.8734
J. A. M. DeBruyne, R. M. Davis, and P. M. Gross [28]	80.05			
E. G. Carter and D. C. Jones [29]	80.00	5.45	1.5012	.8733
A. W. C. Menzies and D. A. Lacoss [30]		5.49		
I. Masson [31]		5.58		
M. Le Blanc and E. Mobnis [32]		5.55		
C. A. Kraus and R. A. Vingee [33]		5.449 to 5.455		
A. J. Ewins [34]		5.58		
J. N. Gifford and T. M. Lowry [35]		5.58	[a]1.50455	
R. Meldrum [36]		5.50		
R. Lorenz and J. Rosen [37]		5.61		
K. Stratton and J. R. Partington [38]		5.85		
J. W. Williams and F. Daniels [39]			1.50449	
J. C. Hubbard [40]			1.49794	
A. R. Martin and B. Collier [41]			[b]1.49312	.87288
M. Wojciechowski	80.094	5.51	1.49807	.87366

[a] n_D^{15}.

[b] n_α^{25}

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DEFORMATION AND YOUNG'S MODULUS OF FIRE-CLAY BRICK IN FLEXURE AT 1,220° C

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ABSTRACT

The plastic and elastic deformations of 17 brands of fire-clay brick were measured. The bricks were primarily of the type intended for high-heat duty and included bricks made by the stiff-mud, dry-press, and handmade methods of manufacture. Measurements were made at 1,220° C on 8 brands as received from the manufacturers and on the 17 brands after reheating at 1,400 and 1,500° C.

Young's modulus of elasticity of specimens in flexure and the modulus of rupture of the bricks as received and also after heating at 1,400° C were determined at 1,250° C.

The results of the deformation tests show that size and quantity of aggregate, ratio of flux to silica, and temperature of preheating before test bear an important relation to the plastic and elastic deformation of these bricks. Young's modulus of elasticity at 1,250° C is only a small fraction of that at ordinary temperatures.

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I. INTRODUCTION

The life of some industrial furnaces depends upon the ability of the firebrick making up the lining to resist deformation at operating temperatures. The use of heat-insulating materials on installations where they have not been formerly used, such as, for example, roofs of open-hearth furnaces and certain types of heat-treating furnaces, has greatly increased the possibility of plastic deformation of the

fire-clay brick exposed directly to the heat of such furnaces. The reason is that insulation results in increasing the average temperature of the firebrick as compared with uninsulated firebrick.

The liability of brick to deform under load at working temperatures was recognized [1] long before insulating materials had gained their present popularity. The present standard method [2] of measuring deformation of fire-clay brick prescribes that the brick be set on end under a load of 25 lb/in.^{2} and heated for 1½ hours at 1,100, 1,300, 1,350, or 1,450° C, depending on the service requirements. The method is such as to preclude results of high precision and therefore was not suitable for this study. It was planned to determine, with a reasonable degree of accuracy, the total deformation (both plastic and elastic) of numerous brands of brick under controlled conditions of temperature, time, and load.

Values for the plastic deformation at 1,000° C of fireclay bricks in flexure were given in an earlier report.[3] The value of similar information obtained closer to the operating temperatures of furnaces is evident; consequently, a study was undertaken in which the temperature of test was 1,220° C. This was found to be the highest temperature at which all specimens could be tested.

The strength and Young's modulus of elasticity for most high-heat duty fire-clay brick at high temperatures are small in comparison with those obtained at room temperature. The resistance of bricks to deformation at high temperatures is probably due largely to the nature and quantity of the glassy bond. The proportion, type, and sizes of the aggregate, as well as the compactness of the entire structure, also have a decided bearing on the total deformation. As the temperature of test of a fire-clay brick is increased above that at which the glassy phase begins to soften, a greater percentage of the total deformation will be due to plastic flow and the resistance to deformation must then depend mainly on the aggregate and the crystal growths. Results of preliminary experimental work indicated that the temperature at which practically all of the test specimens showed sufficient resistance to deformation to permit measurement of their elastic properties was about 1,250° C. The same temperature of test for all materials was desirable so that the data obtained would be comparable.

II. MATERIALS

The fire-clay bricks for this study were left-over samples of the brands discussed in an earlier publication.[4] It was necessary to obtain additional samples of some of the brands.

1. CHEMICAL COMPOSITION

Each sample for chemical analysis was taken from the same brick as the deformation specimen. The results of the analyses are given in table 1. In general, the methods described by Finn and Klekotka,[5]

[1] A. V. Bleininger and G. H. Brown, *The testing of clay refractories with special reference to their load-carrying capacity at furnace temperatures.* BS Tech. Pap. 1 (1910-12) T7.

[2] Standard method of test for refractory materials under load at high temperatures. American Society for Testing Materials Book of Standards for 1936, pt. 2, p. 224.

[3] R. A. Heindl and W. L. Pendergast, *Progress report on investigation of fire-clay bricks and the clays used in their preparation.* BS J. Research 3, 691 (1929) RP114.

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and Lundell and Hoffman [6] were followed. The silica ranges from 48.35 to 81.76 percent, the alumina from 15.01 to 43.81 percent, and the total flux (by difference) from 3.09 to 7.95 percent. This range of values includes most fire-clay bricks.

TABLE 1.—*Chemical composition of firebrick*

Brand	SiO_2	Al_2O_3	Total [1] flux (by difference)	Fe_2O_3+ TiO_2	P_2O_5	Total flux / Total silica
	%	%	%	%	%	
A	57.52	36.70	5.50	3.84	0.05	0.096
B	53.95	38.82	6.89	4.41	.11	.128
C	50.29	43.50	6.05	4.21	.14	.120
D	57.45	36.67	5.64	3.54	.13	.098
E	55.12	39.38	5.34	2.86	.15	.097
F	58.73	35.37	5.54	2.74	.36	.094
G	66.50	30.09	3.23	2.48	.06	.049
H	81.76	15.01	3.09	2.22	.04	.038
I	56.78	35.77	7.03	4.22	.09	.124
J	60.53	31.78	7.43	3.68	.13	.123
K	54.80	38.00	7.02	4.12	.13	.128
L	55.82	36.99	6.89	3.92	.06	.123
M	53.94	37.77	7.95	4.76	.07	.147
N	56.24	38.75	4.75	3.42	.12	.084
P	65.59	26.83	3.34	1.98	.04	.048
Q	48.35	43.81	7.78	2.64	1.68	.161
R	54.89	38.92	5.95	4.22	.09	.108

[1] Difference between the sum of the silica, the alumina, the ignition loss, and 100.

2. PYROMETRIC CONE EQUIVALENTS

The pyrometric cone equivalents (pce or softening points) were determined according to the ASTM [7] standard method, serial designation C24–35. The values are given in the third column of table 2. 15 of the 17 brands of fire-clay brick have a pce of 31 or higher. This indicates that, with one exception, *J*, the materials are of a grade of refractoriness that would preclude appreciable vitrification when reheated at 1,400° C for 5 hours.

3. SIZES OF AGGREGATE AND GROG

The method of obtaining the percentage and size of particles making up the aggregate in the raw batch materials was discussed in an earlier report.[8] For reference purposes the percentage of total particles coarser than a no. 40 sieve (United States Standard Series) for each raw batch of the various brands of brick is given in table 2, column 4. The particles retained on the no. 40 sieve ranged from 19 to 61 percent.

[6] *Analysis of bauxite and of refractories of high alumina content.* BS J. Research **1**, 91 (1928) RP5.
[7] American Society for Testing Materials, Book of Standards for 1936, pt. 2, p. 229.
[8] BS J. Research **3**, 691; (1929) RP114.

TABLE 2.—*Deformation data of fire-clay brick tested at 1,220° C*

Brand	Method of manufacture [1]	Pyrometric cone equivalent	Aggregate retained on sieve no. 40	Deformation of specimens tested as received [2] from manufacturer			Deformation of specimens tested after reheating at 1,400° C for 5 hours				Deformation of specimens tested after reheating at 1,500° C for 1 hour			
				Total after 2½ hr, loaded	Residual after 1 hr, unloaded	Elastic after 60 min [3]	Total after 2½ hr, loaded	Residual after 1 hr, unloaded	Elastic after [3]—		Total after 2½ hr, loaded	Residual after 1 hr, unloaded	Elastic after [3]—	
									5 min	60 min			5 min	60 min
		Cone	%	*Inch*	*Inch*	*Inch*	*Inch*	*Inch*	*Inch*	*Inch*	*Inch*	*Inch*	*Inch*	*Inch*
A	*HM*	33	52				0.0218	0.0171	0.0027	0.0046	0.0134	0.0103	0.0019	0.0031
B	*HM*	32	53				.0141	.0111	.0023	.0030	.0166	.0137	.0018	.0029
C	*DP*	33	59				.0438	.0381	.0040	.0057	.0111	.0086	.0018	.0025
D	*DP*	31–32	43	0.1917			.0142	.0111	.0018	.0031	.0083	.0062	.0012	.0021
E	*DP*	32–33	40				.0241	.0208	.0022	.0033	.0098	.0079	.0012	.0019
F	*SM*	31	40	.0318	0.0282	0.0035	.0096	.0077	.0012	.0019	.0064	.0051	.0008	.0013
G	*HM*	32–33	30	.0206	.0172	.0034	.0102	.0084	.0013	.0018	.0040	.0023	.0009	.0017
H	*HM*	31	22	.0054	.0039	.0016	.0031	.0016	.0008	.0015	.0009	.0000	.0005	.0009
I	*HM*	31	51				.0472	.0398	.0046	.0074	.0214	.0179	.0024	.0035
J	*SM*	30	31				.0360	.0323	.0024	.0037	.0229	.0192	.0023	.0037
K	*SM*	32	44				.0296	.0258	.0027	.0038	.0150	.0121	.0013	.0029
L	*DP*	33	44	.0986			.0263	.0230	.0023	.0033	.0139	.0111	.0017	.0028
M	*HM*	33	47				.0192	.0167	.0020	.0025	.0120	.0091	.0020	.0029
N	*SM*	32	43	.0480	.0439	.0040	.0080	.0062	.0011	.0022	.0060	.0048	.0008	.0012
P	*SM*	30–31	19	.0048	.0031	.0017	.0035	.0024	.0007	.0011	.0022	.0003	.0005	.0019
Q	*DP*	33	61				.0574	.0517	.0029	.0057	.0190	.0150	.0031	.0040
R	*HM*	32–33	31	.0086	.0063	.0022	.0062	.0044	.0009	.0018	.0066	.0045	.0012	.0021

[1] *HM*, *SM*, *DP* refer to handmade, stiff-mud, dry-press processes of manufacture, respectively.
[2] With the exception of those shown, specimens ruptured within 15 minutes after application of load. *D* and *L* failed after 80 and 50 minutes, respectively.
[3] Representing the elastic recovery at the end of 5 minutes and 60 minutes after unloading.

4. POROSITY

The porosity determinations were made in accordance with the test method adopted by the American Ceramic Society,[9] except that the specimens were boiled for 5 hours and permitted to cool overnight. The specimens (1 by 1 by 2 in.) were cut from the bars after deformation tests had been completed. The results given in table 3 are for reference purposes only.

TABLE 3.—*Modulus of rupture, Young's modulus of elasticity, and porosity of fire-clay brick tested at 1,250° C*

Brand	Porosity		As received from manufacturer		After reheating at 1,400° C for 5 hours	
	As received [a]	After reheating at 1,400° C	Modulus of rupture	Modulus of elasticity	Modulus of rupture	Modulus of elasticity
	%	%	lb/in.²	1,000 lb/in.²	lb/in.²	1,000 lb/in.²
A	27.7	22.0	85	77	520	233
B	22.0	20.4	200	174	765	372
C	21.6	20.0	55	76	500	238
D	16.4	15.3	230	159	860	256
E	16.2	15.6	220	144	945	361
F	14.4	9.6	830	277	1,450	535
G	31.8	29.0	720	201	870	275
H	36.6	30.4	640	254	905	621
I	24.8	18.9	145	86	485	130
J	16.1	9.6	[b] 195	[b] 134	380	147
K	21.0	18.0	105	116	700	309
L	17.0	12.0	195	150	600	228
M	22.1	20.5	150	137	710	347
N	20.0	12.7	1,060	314	1,600	742
P	25.2	24.0	2,045	522	1,850	975
Q	16.3	14.5	[c] 650	[c] 156	130	233
R	29.8	22.0	445	229	1,170	602

[a] Specimens used had been tested at 1,250° C for deformation.
[b] Tested at 1,150° C.
[c] Tested at 1,100° C.

III. SPECIMENS

The specimens for comparing the effect of heating at different temperatures on plastic deformation represent only one brick of each brand because of the wide variation in certain properties between firebrick of the same brand, which has been discussed by Heindl.[10] The specimens measured 1 by 1 by 9 in. Two of the 1- by 9-in. surfaces of each specimen were outside surfaces of the brick. That surface of the specimen which had been a portion of the 9- by 2½-in. surface of the brick was removed by grinding. One of the specimens in each case was set aside for testing without reheating, a second was reheated at 1,400° C for 5 hours, and the third at 1,500° C for 1 hour.

In addition, specimens from more than one brick were tested, after reheating at 1,400° C for 5 hours, to obtain data comparing variation in total deformation between bricks of the same brand.

For Young's modulus of elasticity and strength, the specimens do not necessarily represent either one brick or edge specimens as was the case with the plastic-deformation studies.

[9] J. Am. Ceram. Soc. 11, 456 (1928).
[10] A discussion of thermal spalling of fire-clay brick with relation to Young's modulus of elasticity, thermal expansion and strength. Am. Ref. Inst. Tech. Bul. no. 58 (May 1935).

IV. METHODS OF TESTING

1. DEFORMATION

The furnace and equipment for making measurements of the plastic deformations of firebrick have been described by Heindl and Pendergast.[11] The specimens were tested over an 8-inch span. The stress at the extreme fiber, exclusive of the weight of the loading clevis and specimen, was 6 lb/in^2. The temperature of the furnace was maintained at approximately 1,220° C (average of readings of two thermocouples) during the test and for 1 hour immediately preceding the application of the load. After the load was applied, gage readings were taken for a 150-minute period, the first four readings being taken at 5-minute intervals and the balance at 10-minute intervals. At the end of that time the load was removed and readings were taken at periodic intervals for 60 minutes to measure the elastic recovery of the material.

2. YOUNG'S MODULUS AND STRENGTH

The apparatus used for determining Young's modulus of elasticity as well as the transverse strength was the same as that used for determining the total deformation. In the present instance the furnace temperature as indicated by one thermocouple close to the specimen was 1,250° C. The specimens were under load for 5-minute periods and were permitted to recover after releasing each load for a 15-minute period. In general, the same types of curves were obtained as are illustrated in an earlier report,[12] although the time intervals for loading and unloading and the temperature of test were different.

The modulus of rupture was obtained after completion of the elastic measurements by gradually increasing the load until rupture occurred.

3. MICROSCOPIC ANALYSIS AND STRUCTURE

An examination with the petrographic microscope was made of 9 of the 17 brands of bricks. Thin sections were prepared from the same brick from which plastic-deformation specimens were taken; a section was made from the bricks as received from the manufacturer, a second and third after reheating at 1,400° C and at 1,500° C, respectively. The primary purpose of this examination was to obtain information regarding the content of glass and the extent and development of mullite due to the reheating.

The structure of each brand of brick was studied with 10-power binoculars. The purpose of this examination was to obtain information as to compactness of structure and type of aggregate as well as the general appearance of the bonding clay with the aggregate.

V. RESULTS AND DISCUSSION

1. DEFORMATION OF FIRE-CLAY BRICK

The values for total deformation of the bricks tested are given in table 2. The total deformation under load includes both the elastic and plastic deformations. After removal of the load a certain amount

[11] *Young's modulus of elasticity at several temperatures for some refractories of varying silica content.* J. Research NBS **13**, 851 (1934) RP747.

[12] *Progress report on investigation of fire-clay bricks and clays used in their preparation.* BS J. Research **3**, 691 (1929) RP114.

of recovery takes place. The deformation remaining at the end of 1 hour is termed "residual deformation" and represents largely plastic deformation which took place during the test, while the recovery after removal of the load is termed "elastic deformation." These data show that a great portion of the elastic recovery takes place within the first 5 minutes after removal of the load.

Figure 1 shows typical curves of the deformation obtained on three brands of brick under load for 150 minutes. For all bricks the deflection increases with time. With removal of the load a fairly rapid recovery takes place immediately as indicated by the break in the curves at 150 minutes. The recovery thereafter continued to the end of the test but at a gradually reducing rate.

(a) EFFECT OF PARTICLE SIZE

The percentage of aggregates or particles in the raw brick batches not passing a United States Standard Sieve no. 40 are given in table 2. The range is from 19 to 61 percent, with the tendency for the highly siliceous clay batches to contain the lower percentages and the high flint clay batches to contain the higher percentages of aggregate.

Analysis of the deformation values obtained on 1 specimen of each of the 17 different brands reheated at 1,400° C indicated a direct relation between percentage of particles coarser than a no. 40 sieve and the total deformation. The coefficient of correlation,[13] 0.72, shows the existence of such a relation, which apparently ceases to exist after the specimens have been reheated at 1,500° C, owing to the reaction between the bond clay and the aggregate. The coefficient of correlation in this case was 0.14.

(b) EFFECT OF METHOD OF MANUFACTURE

Firebrick brands *E, F; D, N;* and *L, K* were furnished by three manufacturers. The raw batch for each pair was of the same composition, but the method of forming was different; that is, brands *F, N,* and *K* are stiff-mud bricks, whereas, *E, D,* and *L* are dry-pressed. However, the processes of forming *L* and *K* are somewhat modified. Consequently, the structure of *K* does not correspond to that of the typical stiff-mud brick. In the case of *F* and *N* the deformations are much less than for the corresponding brands *E* and *D* made by the dry-press process. Although L_{14} (brand *L* reheated at 1,400° C)[14] and K_{14} represent the dry-press and stiff-mud processes, respectively, there is no noticeable difference as far as appearance of the structure is concerned. This similarity in structure may account for the not great dissimilarity in deformation properties. Figure 2 shows F_{14}, a typical stiff-mud structure and E_{14}, a dry-pressed structure; R_{14} is a handmade brick. Figure 3 shows L_{14} as a "modified" dry-press brick and K_{14} as a "modified" stiff-mud brick, both from the same raw batch, and I_{14} as a loosely bonded handmade brick containing a large amount of aggregate.

Though not conclusive, the data (table 2) in general indicate that bricks of the dry-press type have uniformly high deformations; the stiff-mud type, with one exception, low deformations and the handmade deformations intermediate of the first two types.

[13] Manual for Interpretation of Refractory Test Data. ASTM Standards on Refractory Materials (Feb. 1935).

[14] In this report the heat treatment any specimen received before test is indicated thus: *L*, as received; L_{14}, reheated at 1,400° C; L_{15}, reheated at 1,500° C.

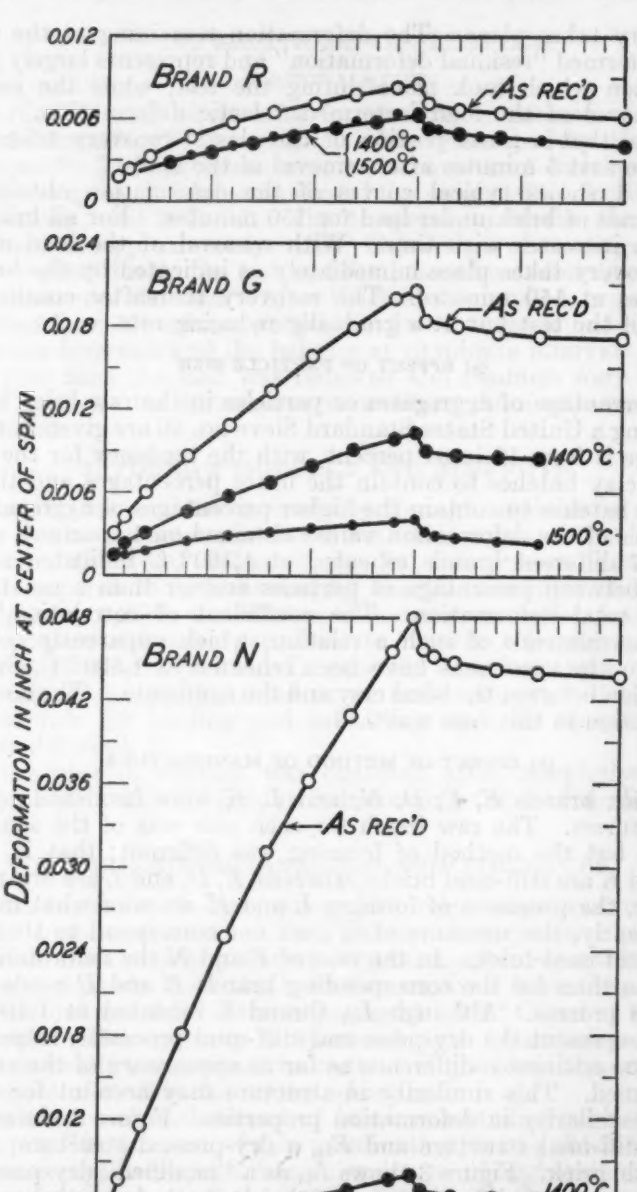

FIGURE 1.—*Effect of heat treatment on the deformation of different types of fire-clay brick.*

Deformation under load and recovery after removal of the load of fire-clay brick brands *R*, *G*, and *N* as received from the manufacturer and after reheating at 1,400° C and at 1,500° C as noted adjacent to each curve.

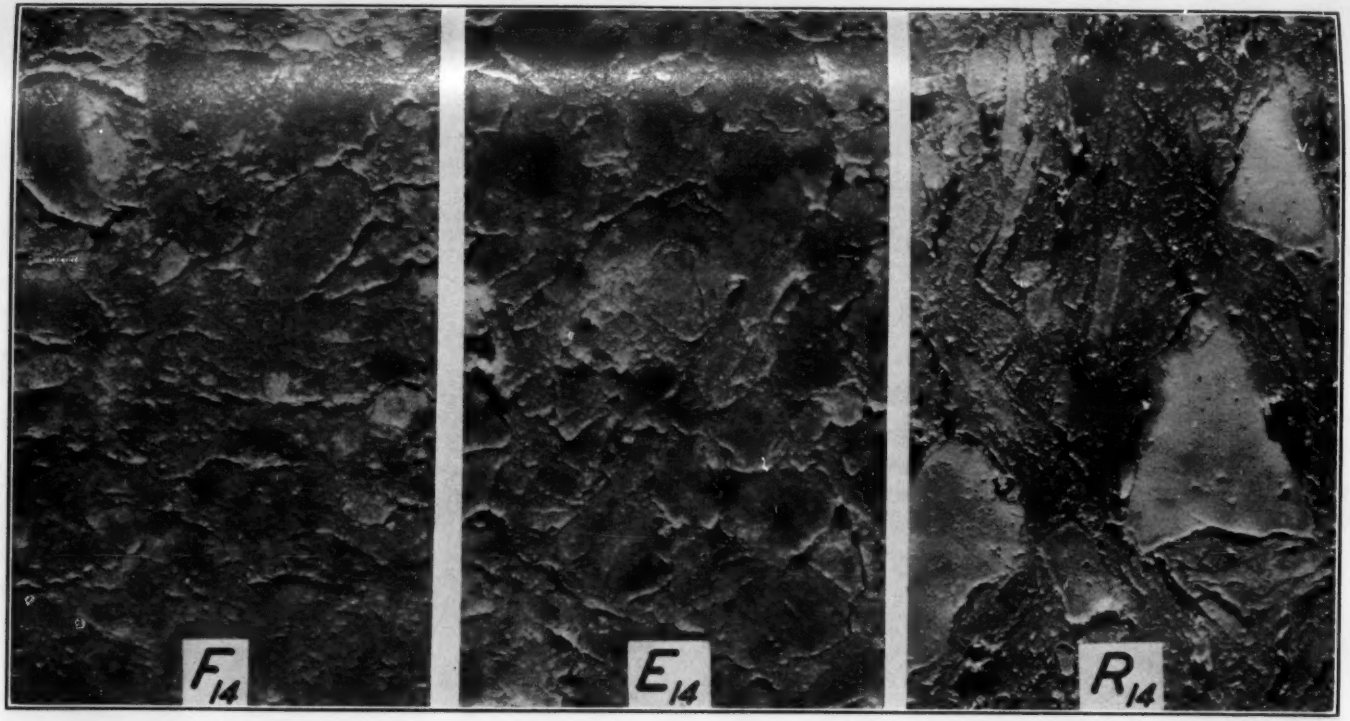

FIGURE 2.—*Semipolished section* ($\times 12$) *of firebrick brands F, E, and R reheated at 1,400°* C.

Brands *E* and *F* have the same composition and a very uniform structure, but the former, manufactured by the dry-press process, is considerably more open than the latter, which is manufactured by the stiff-mud process. *R*, manufactured by the hand-made process, shows a structure filled with more or less parallel channel pores.

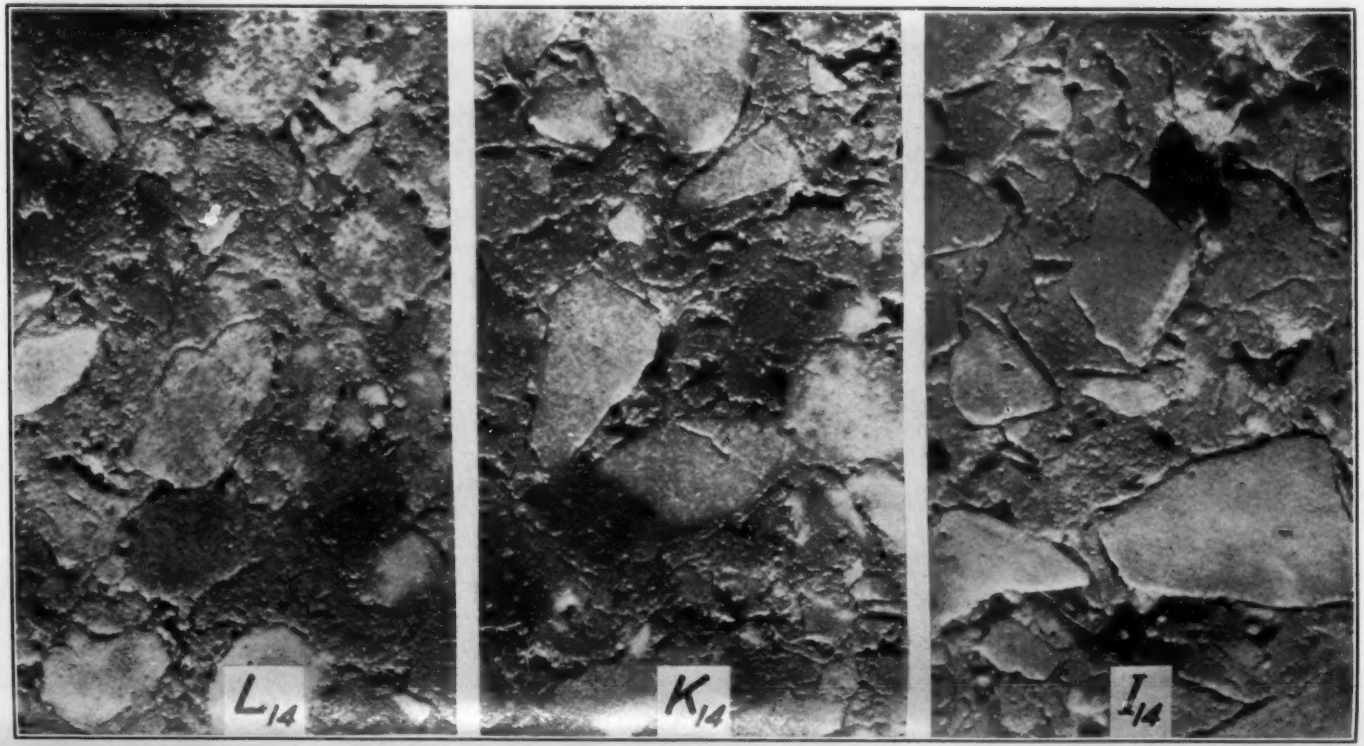

FIGURE 3.—*Semipolished sections* (× *12*) *of fire-clay brick brands L, K, and I after reheating at 1,400° C.*

L and *K* have the same composition. Although manufactured by modified dry-press and stiff-mud processes, no significant differences in structure were apparent. *I*, formed by the hand-made process, shows the flint-clay particles to have shrunk considerably more than the bond clay, which is not so apparent with *L* and *K*.

L and K have the same composition. Although manufactured by modified dry-press and stiff-mud processes, no significant differences in structure were apparent. J, formed by the hand-made process, shows the flint-clay particles to have shrunk considerably more than the bond clay, which is not so apparent with L and K.

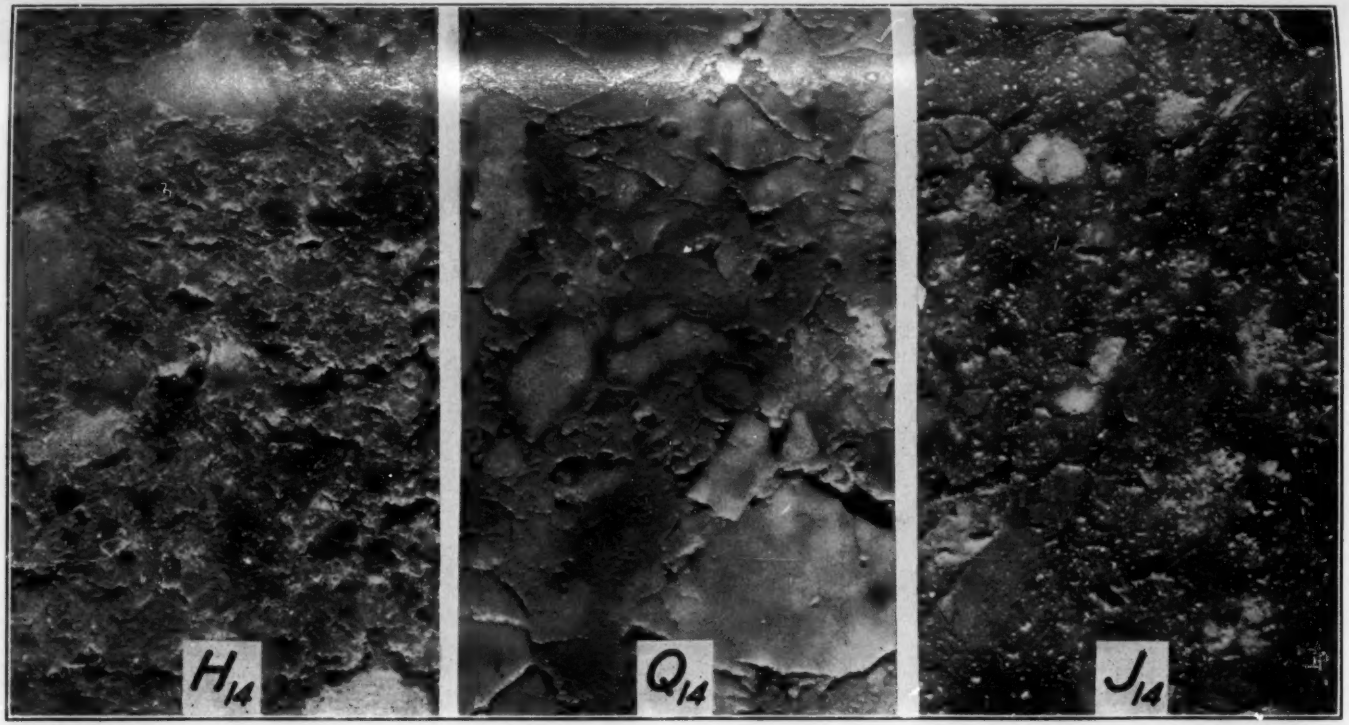

FIGURE 4.—*Semipolished sections* ($\times 12$) *of firebrick brands H, Q, and J after having been reheated at 1,400° C for 5 hours.*

H_{14}, a highly siliceous fire-clay brick with a skeleton of quartz particles, has very little deformation; Q_{14}, made from a single clay, has a high alumina content and a very high deformation when tested at 1,220° C. J_{14}, less refractory than either H or Q, is almost a monolithic structure and has a high deformation.

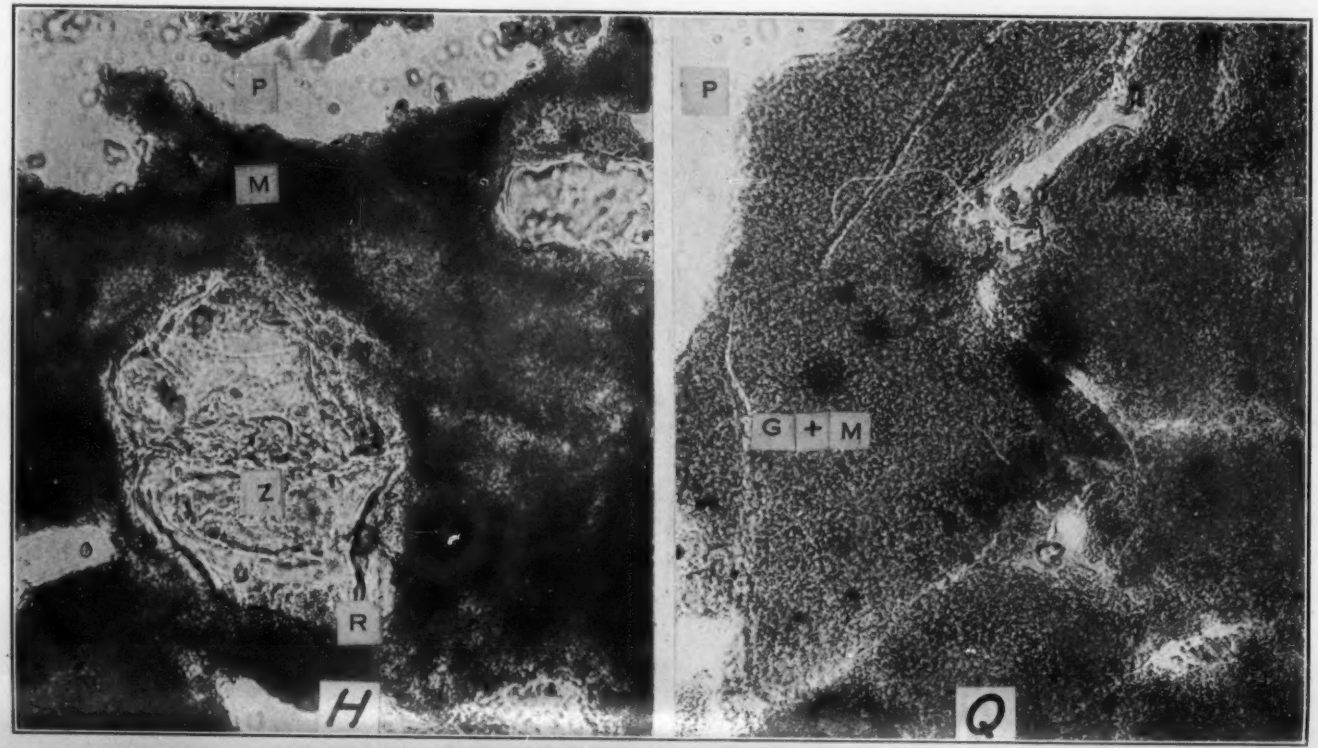

FIGURE 5.—*Section of firebrick brands H and Q (ordinary light, ×430) as received from the manufacturer.*

H shows quartz crystals (small letter *Z*) with solution rim (*R*), appreciable development of mullite (*M*) in the clay bond, and very little glass in the area designated *M*. The high glass (light background *G*) content in the bonding material, almost complete absence of quartz crystals, and meager mullite (dark specks *M* in field of *G*) crystallization are noted in brand *Q*. The light areas designated *P* in both sections are pores.

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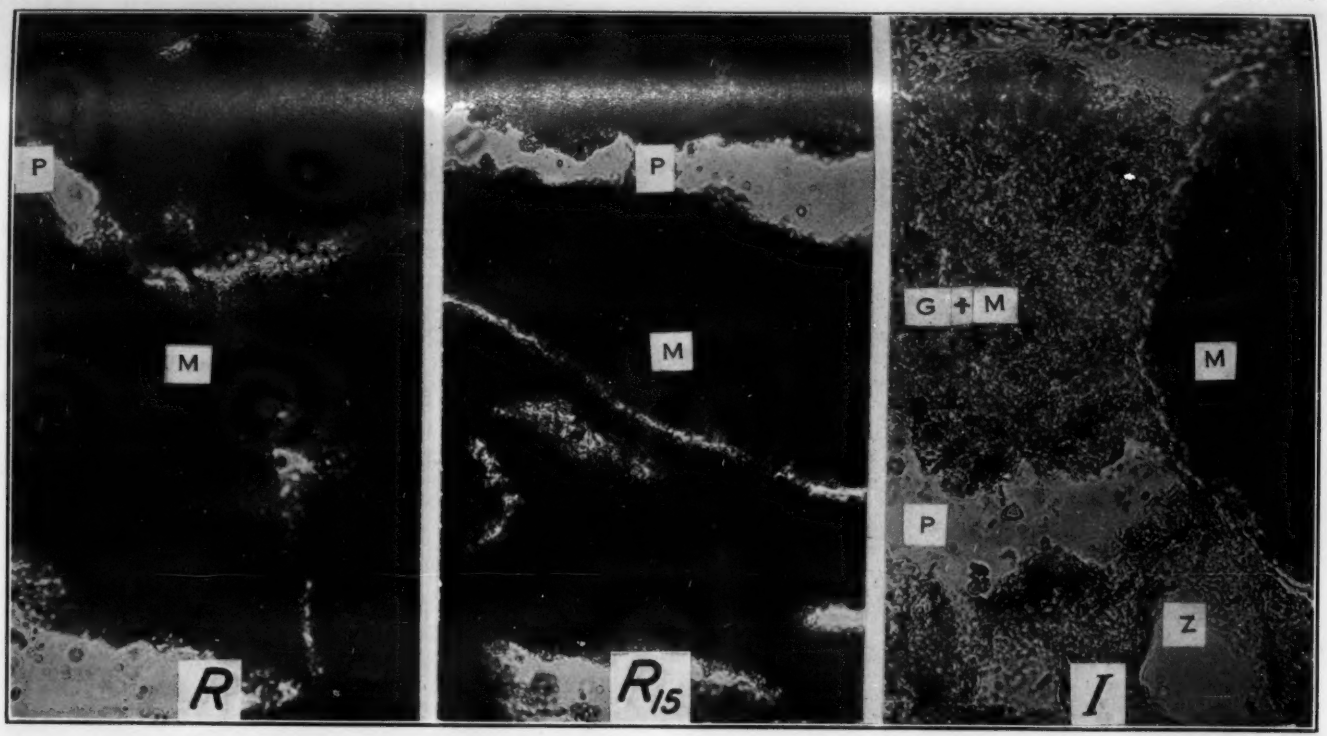

FIGURE 6.—*Section of firebrick brand R as received, and after heating at 1,500° C (R_{15}) and brand I as received (ordinary light, ×430).*

Both *R* and R_{15} show very little glass (only in evidence along edges of pores *P*), with mullite abundant (as indicated by dark areas *M*). R_{15} shows that reheating has changed the structure very little. Section *I* in comparison shows much glass (light background of *G*+*M*) with only a small amount of mullite (dark specks *M* in field of *G*+*M*) in the bond but an appreciable amount in the flint-clay grain (dark area *M*), possibly due to preheating before being compounded in the brick batch. Some quartz grains (*Z*) and pores (*P*) are in evidence. *R* has a low deformation and that of *I* is very high.

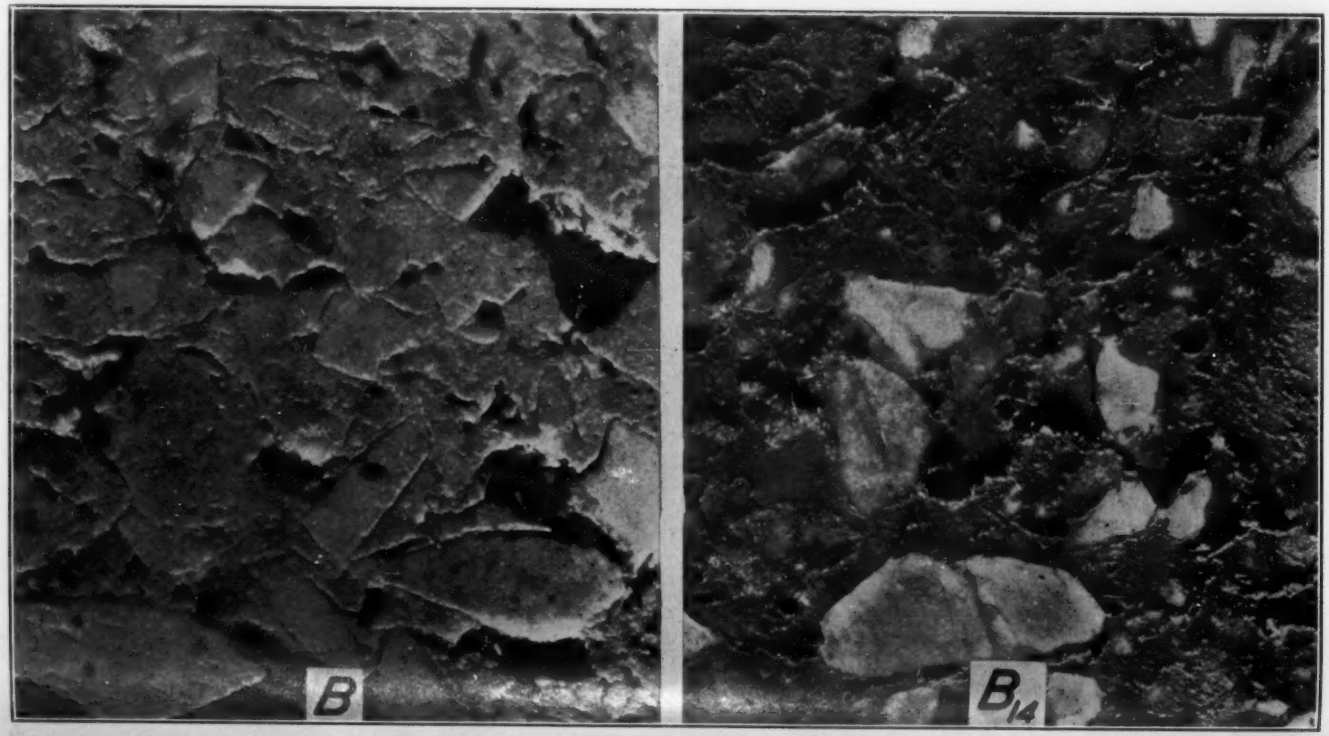

FIGURE 7.—*Semipolished section (×12) of fire-clay brick brand B as received from manufacturer and also after heating at 1,400° C.*

The effect of the reheating on the structure is evidenced by the welding of the semiflint-clay particles and bonding clay forming a monolithic structure in which flint-clay particles are fairly tightly embedded. The monolithic structure is filled with blebs.

(c) EFFECT OF TOTAL FLUX AND TOTAL SILICA

The data obtained are in agreement with the well-known fact that highly siliceous fire-clay bricks have less deformation at high temperatures than do those bricks containing more alumina. The ratio of total flux to total silica is given in table 1. It is to be expected that up to a certain point a high percentage of flux will tend to lower the viscosity of the glass present in a refractory and this in turn will tend to increase the deformation.

A reasonably good relation was noted between total deformations obtained on bricks reheated at 1,400° C and the ratio of total flux to total silica. Such a relation is also indicated by the coefficient of correlation which was found to be 0.84. Figure 4 compares the structure of H_{14}, a highly siliceous brick (81.76 percent of SiO_2) with a low ratio of flux to silica (0.038), and Q_{14} containing much less silica (48.35 percent) and a rather high flux to silica ratio (0.161). These two brands represent the extremes in total deformation. J_{14} has a low pce (30) and a fairly high flux to silica ratio (0.123). Since the petrographic examination of J_{14} showed mullite to be in abundance, the deformation is not as great as that in some of the others having a less-dense structure, as for example Q_{14}. Figure 5 also compares brands H and Q but under high magnification. H shows much less glass than Q and a high percentage of mullite. The bonding material in Q, on the other hand, is very glassy with mullite present in small quantities only.

(d) EFFECT OF HEAT TREATMENT

Table 2 gives data on 8 specimens as received and on 17 specimens which had been reheated at 1,400° C and a second series of 17 at 1,500° C. Nine specimens set up for test as received failed before their deformations could be observed. After reheating, however, all specimens could be tested. Only the typical examples for which curves are shown in figure 1 will be discussed.

Brand R does not deform greatly when tested as received nor does the extent of that deformation change greatly after reheating the specimens at either 1,400 or 1,500° C. Brand G, as received, has a moderately high deformation; after the reheating at 1,400° C the deformation decreases to about one-half and after the reheating at 1,500° C to about one-fifth of that of the as received specimen. Brand N, as received, had a high deformation, but after the reheating at 1,400° C its deformation was only a small fraction of that of the as received specimen and showed comparatively little further change after reheating at 1,500° C.

There are several reasons why brand R has high resistance to deformation. The petrographic examination showed that R, as received, contained very little glass and that mullite was in abundance. Reheating at 1,400° C and reheating at 1,500° C somewhat increased the content of mullite. Figure 6 shows brand R as received and after reheating at 1,500° C (R_{15}). An abundance of mullite is indicated in both cases by the dark (opaque) areas. Brand R contains many more or less elongated parallel (channel) pores as may be seen in figure 2, (low magnification of R). These pores are parallel to the direction of the applied load during the deformation test; therefore, it is believed that they did not have an appreciable effect on the deformation. R_{14} (fig. 2) shows also the tendency for the bond and aggregate to shrink toward one another; that is, the shrinkage is such that the bond

FIGURE 7.—*Semipolished section* (×12) *of fire-clay brick brand B as received from manufacturer and also after heating at 1,400° C.*

The effect of the reheating on the structure is evidenced by the welding of the semiflint-clay particles and bonding clay forming a monolithic structure in which flint-clay particles are fairly uniformly embedded. The monolithic structure is filled with pores.

clay and aggregate remain in fairly intimate contact. The narrow-channel pores in some cases are adjacent to the coarse angular clay particles, which may give an impression that shrinkage of the aggregate has been greater than the bonding material. But this is not the case, as was proved by an examination of the full-size specimen. The closing together of bond and aggregate naturally causes a body to be more resistant to deformation. Furthermore, *R* contains comparatively little coarse aggregate (31 percent) and the flux to silica ratio is not high.

Brand *G* (fig. 1) is of the highly siliceous type of brick. It has a low flux to silica ratio and a low percentage of coarse aggregate. The bond and aggregate are in close contact and the brick has a fairly compact but granular appearance.

An examination with the binoculars of brand *N*, also referred to in figure 1, showed a well-bonded, compact, and dense structure. There was a slight tendency for some of the aggregate to shrink from the bond. The percentage of coarse aggregate was intermediate between the extremes for all brands of bricks. The petrographic examination showed a very high glass content and some mullite in the original brick. The glass decreased and the mullite needles increased in size and quantity with the higher heat treatments. A few grains of quartz were observed. The decrease in deformation with the heat treatments was undoubtedly due to the decrease in glass and increase in quantity of mullite crystals.

Figure 7 shows the effect on structure after reheating at 1,400° C a loosely bonded handmade brick. This brick contains a high percentage of coarse aggregate which has an appearance of not being well mixed with the bond. Twenty-two percent [15] of the aggregate was retained on a no. 10 sieve. Because of the open structure, which is emphasized by the tendency of some of the aggregate to shrink from the bond, the as received specimen failed before the deformation could be observed. The bond clay had a pce of 26 and the petrographic examination showed some mullite needles and an appreciable discoloration of the glass due to a fairly high content of iron. After reheating at 1,400° C (B_{14}) the deformation could be readily measured and it was rather low compared with several of the others which had approximately the same ratio of flux to silica. This is difficult to explain. An abundance of mullite and the tightening and welding of the structure (see fig. 7) may be the cause of the comparatively low deformation. However, after the reheat at 1,500° C the deformation was actually greater which, although small, is the reverse order from that shown by other brands. Petrographic examination showed many blebs and many long needles of mullite in the glass adjacent to quartz particles. The specimen was highly stained with iron and many particles appeared overfired or vitreous.

Figure 8 shows the effect of heating brick made from one clay (all flint clay) at successively higher temperatures. Brand *Q* had the greatest percentage of aggregate (61 percent) retained on the no. 40 sieve. The aggregate, largely of medium size, was well distributed, angular, and formed the skeleton of the brick. The structure was compact, as evidenced by the porosity of 16 percent. The absence of low fluxing bonding materials was indicated by the pyrometric-cone

[15] *Progress report on investigation of fire-clay bricks and the clays used in their preparation.* BS J. Research 9, 691 (1929) RP114.

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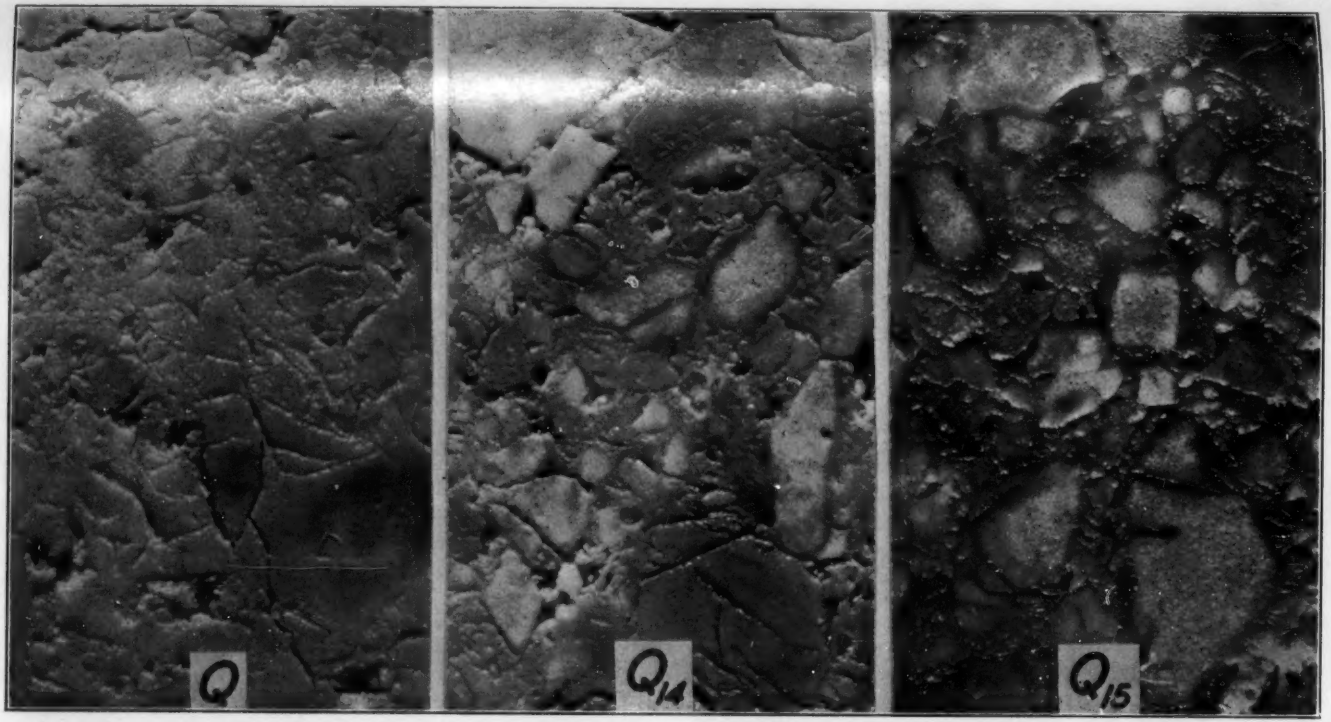

FIGURE 8.—*Semipolished sections* (×12) *of firebrick brand Q (made from one clay only) as received from the manufacturer and after reheating at 1,400° C* (Q_{14}) *and at 1,500° C* (Q_{15}).

Q is very compact, but lack of bonding strength is indicated by many hairlike cracks between the closely packed particles. Q_{14} shows shrinkage of coarsest particles to be slightly greater than the fine, and the hairlike cracks in the finer aggregate have disappeared. Q_{15} shows both coarse and fine material drawn closely together, and the whole appears well bonded.

FIGURE 9.—*Sections of firebrick brand I as received (I) and after reheating at 1,500° C (I_{15}) (crossed nicols, ×430).*

The glassy bond plus mullite (*G+M*) with quartz particles (*Z*) and the mullite (*M*) in the flint-clay particles are shown in section *I*. Almost complete absence of quartz and high content of mullite is shown in section I_{15}. Pores are indicated (*P*).

equivalent of 33 (refractoriness of both aggregate and bonding particles). These facts, together with the high deformation shown by *Q*, indicate that the brick was not well bonded as is supported by figure 8. After reheating at 1,400° C the coarse aggregate shrinks slightly more than the fine, but the latter appeared to have become well bonded. After reheating at 1,500° C the structure was drawn together as a whole; that is, both the aggregate and fines generally shrink together and become well bonded. These changes in structure with reheating can readily account for the greatly reduced deformation after reheating. *Q* is outstanding also in that it has an exceptionally high P_2O_5 content.

Photomicrographs of brand *I*, as received and after reheating, are shown in figures 3, 6, and 9. In figure 3, I_{14} shows a high percentage of coarse aggregate and the shrinkage of the flint-clay particles from the bond clay is pronounced. The aggregate makes a fairly complete skeleton, but there are many pores and the whole has a crumbly and spongy appearance. As might be expected, the deformation is high. *I* in figure 6 was taken with ordinary light and represents the same thin section as *I* in figure 9, except that the latter was taken with crossed nicols. High-glass content in the bond clay and mullite in the flint-clay particle are indicated. Pore space and small quartz crystals may also be seen. I_{15} shows the whole to be a mass of mullite needles, and glass is not much in evidence. As a result the deformation of *I* has greatly decreased.

2. RELATION OF PARTICLE SIZE, RATIO OF FLUX TO SILICA, HEAT TREATMENT, AND DEFORMATION

Figure 10 (lower) shows the total deflection of specimens reheated at 1,400° C and (upper) reheated to 1,500° C as a function of particle size and ratio of flux to silica. In these graphs the highly siliceous bricks appear in the lower left-hand corner and those containing the most alumina appear near the upper right. Although there are some exceptions, the limited number of materials tested do indicate a trend; that is, with increased quantities of coarse aggregate and a high ratio of flux to silica, high deformations are shown. However, after heating at 1,500° C (upper graph) the effect of particle size is apparently eliminated and the value of the ratio of total flux to total silica is the deciding factor as to the extent of the total deformation (coefficient of correlation 0.84) as well as the plastic flow as shown by the data on plastic flow in table 2.

The values for deformation, indicated by length of lines, in the lower graph are averages of all specimens of each brand reheated at 1,400° C; those for 1,500° C are the result of one test only. However, the results of tests for the one specimen (1,400° C reheat) cut from the same brick as that reheated at 1,500° C gives a similar relation. Furthermore, plotting the plastic or residual deformation data in lieu of the total deformation results in a similar type of graph.

Values for deformation obtained for several specimens from the same brand of brick reheated at 1,400° C are given in table 4. The purpose is to show the variation in deformation between specimens of different bricks of the same brand as well as between duplicate specimens of the same brick.

The glassy bond plus mullite (*G*+*M*) with quartz particles (*Z*) and the mullite (*M*) in the flint-clay particles are shown in section *I*. Almost complete absence of quartz and high content of mullite is shown in section I_{15}. Pores are indicated (*P*).

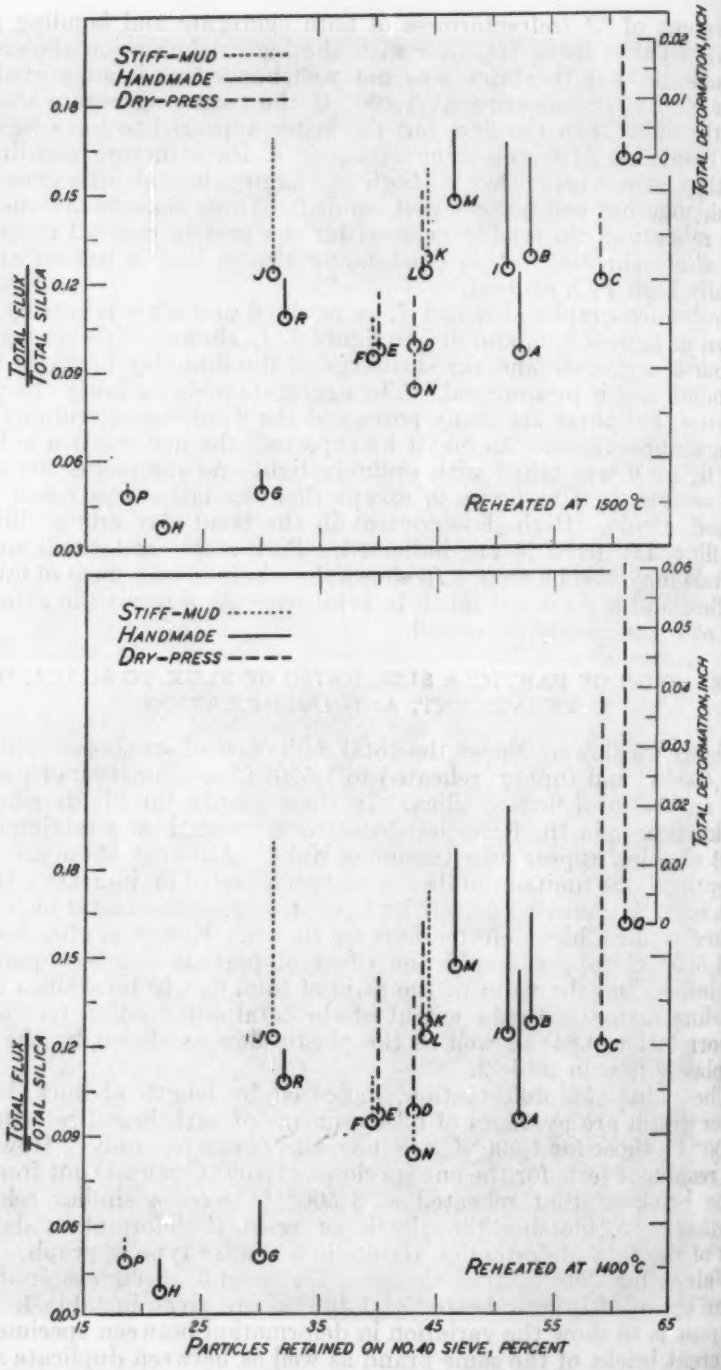

FIGURE 10.—*Deflection of 17 brands of fireclay brick after 2½ hours as a function of particle size and ratio of total flux to total silica.*

The specimens were reheated at 1,400° C and at 1,500° C and tested at 1,220° C. The vertical lines indicating the extent of the deformations may be visualized as perpendicular to the plane of the paper. In the lower graph a trend is indicated, namely deformations increase with quantity of aggregate and increasing ratio of flux to silica. After reheating at 1,500° C the particle size is apparently no longer an important factor in resistance to deformation.

TABLE 4.—*Multiple determinations of total deformation at 1,220° C of fire-clay brick after heating 5 hours at 1,400° C*

[Determinations made at 1,220° C]

Brand and sample [a]	Total deformation after 2½ hr	Brand and sample [a]	Total deformation after 2½ hr	Brand and sample [a]	Total deformation after 2½ hr
	Inch		*Inch*		*Inch*
A1	0.0285	*F1*	0.0095	*M1*	0.0192
A2	.0218	*F2*	.0059	*M2*	.0273
A3	.0250	*F3*	.0075	*M3*	.0122
B1	.0181	*G1*	.0102	*N1*	.0080
B2	.0141	*G2*	.0082	*N2*	.0059
B3	.0225	*G3*	.0101	*N3*	.0067
C1	.0438	*H1*	.0081	*P1*	.0035
C2	[b].0709	*H2*	.0031	*P2*	.0049
				P3	.0036
D1	.0155	*I1*	.0472		
D1	.0142	*I2*	.0346	*Q1*	.0574
D2	.0329	*I3*	.0325	*Q2*	[b].0643
D3	.0146				
		J1	.0360	*R1*	.0537
E1	.0125	*J2*	.0364	*R1*	.0442
E1	.0127	*J3*	.0264	*R2*	.0472
E2	.0236			*R2*	.0513
E2	.0214	*K1*	.0296	*R3*	.0500
E3	.0202	*K2*	.0163	*R3*	.0623
E3	.0227	*K3*	.0206	*R4*	.0517
E4	.0313			*R4*	.0486
E4	.0429	*L1*	.0157	*R5*	.0559
E5	.0241	*L1*	.0269	*R6*	.0548
E6	.0200	*L2*	.0263		
		L3	.0091		

[a] The letter refers to the brand, the number following refers to the specimen. Different numbers indicate specimens were obtained from different bricks of the same brand; duplicate numbers indicate different specimens taken from the same brick.

[b] Specimens failed before 2½-hour period elapsed; value extrapolated.

3. YOUNG'S MODULUS AND STRENGTH

Table 3 gives the modulus of elasticity of fire-clay brick in flexure and the modulus of rupture and porosity for the materials as received and after reheating at 1,400° C. Brands *J* and *Q* as received were tested at 1,150 and 1,100° C, respectively, because, as already stated, they failed shortly after application of the load at 1,250° C. The values represent the average of two or more determinations.

The results show that the modulus of elasticity of most of the bricks is quite low at 1,250° C and for a number of brands is considerably less than 10 percent of the value obtained at room temperature.[16] The highly siliceous type show the least change. The strength values are also appreciably less than those obtained at ordinary temperatures. These low values are evidently due to the partial softening of the glass.

Reheating the specimens at 1,400° C greatly increased both Young's modulus of elasticity and the modulus of rupture. The increase in quantity and size of mullite crystals and decrease in glass, as indicated by the microscopic examinations, is believed to be the major cause for this change.

VI. SUMMARY AND CONCLUSIONS

The total deformations (plastic and elastic) of 17 brands of fire-clay brick in flexure at 1,220° C were determined after reheating at 1,400 and 1,500° C. Similar information was obtained on 8 of the 17 brands

[16] *Progress report on investigation of fire-clay bricks and the clays used in their preparation.* BS J. Research 3, 691 (1929) RP 114.

as received from the manufacturer, the remaining 9 having failed before deformation data could be obtained. Young's modulus of elasticity in flexure and the modulus of rupture were determined at approximately 1,250° C on the bricks as received and also after heating at 1,400° C. The deformations were obtained with a stress of approximately 6 lb/in.^{2} applied midspan to a 1- by 1- by 9-inch specimen on an 8-inch span. The modulus of elasticity and strength were determined on the same type of specimen and span; the load increments were varied according to strength of the specimen.

The following results were obtained:

1. The total deformation of specimens heated at 1,400° C increased in general with increase in quantity of particles in the raw brick batches retained on a United States Standard Sieve no. 40.

2. In general, the data indicate that bricks of the dry-press type have uniformly high deformations, the stiff-mud type, with one exception, low deformations, and the handmade type have deformations intermediate of the range of the two other types.

3. Bricks of the lowest ratio of total flux to total silica have much less deformation than those having the highest ratio.

4. The deformation decreased greatly in most cases when the specimens were given preliminary reheat treatments at 1,400 and at 1,500° C. With one exception, the bricks high in silica showed the least change in deformation after the reheat treatments. The petrographic examination showed successive decreases in glass content and increases in the crystallization of mullite with reheating. Specimens showing low deformation when tested as received were either of the siliceous type or contained considerable quantities of mullite crystals. Much glass was present in those showing high deformations.

5. Although there are exceptions, the total deformations of the limited number of materials tested do indicate a trend; that is, deformations increase as the quantity of coarse aggregate and ratio of flux to silica increase. After having been reheated at 1,500° C, particle size is apparently no longer an important factor.

6. Young's modulus of elasticity of specimens in flexure as received from the manufacturer was less than 200,000 lb/in.^{2} for 11 of the 17 specimens. It was about twice as great after reheating at 1,400° C. The strength of the reheated specimens also increased greatly in most cases.

The authors express appreciation to G. R. Shelton for the microscopic analyses, making the photographs, and suggestions regarding their interpretation, and to E. H. Hamilton for the chemical analyses.

WASHINGTON, July 13, 1937.